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SOCIETY of ECONOMIC GEOLOGISTS

OFFICERS FOR 1945

SPHALERITES FROM WESTERN CANADA.[1]

H. V. WARREN AND R. M. THOMPSON.

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ABSTRACT.

A study of 164 samples of sphalerite, of which 122 are from Western Canada, has confirmed the results of other workers in this field, and particularly those of Stoiber.

Western Canada, as a metallogenetic province, is high in gold and tin, but is low in gallium, germanium, and vanadium. Within Western Canada there are many definite districts, each of which tends to show a characteristic minor element assemblage.

The relative abundance of the various minor elements which have been studied is discussed, and the characteristic distribution of some of these minor elements in a few important areas is noted.

As an important by-product of these studies, an apparent relationship is shown between the depth to which orebodies containing native gold and silver persist and the amount of manganese present in associated sphalerite.

INTRODUCTION.

SPECTROGRAPHIC examinations of samples of sphalerite taken from many localities have shown that most of these samples contain, in addition to zinc, sulphur, and iron, small amounts of several other elements. These elements, in general, are quantitatively of minor importance and are usually referred to as minor elements. Occasionally these minor elements are of economic importance, but their chief value at the present time seems to be that it may be possible, by studying their occurrence and distribution, to add a little to our knowledge of the genesis of ore deposits.

The authors have also found an additional use for these minor elements which, incidentally, occur not only in sphalerite, but also in other minerals. This new use involves utilizing the fact that some elements and minerals which are of economic importance are hard to discover and determine in the field, but are distributed in minute amounts in other minerals which can more readily be found and determined.

It happens that in Western Canada there is evidence that tin, albeit in modest amounts, is widespread. Until 1943, however, no commercial deposit had been found, although tin was, and still is, being produced as a by-product of the Sullivan ore. It was in an effort to assist in finding a commercial tin deposit that the authors decided to examine spectroscopically several hundred specimens of some of the commoner minerals, which can readily be found and recognized in the field, to ascertain whether one or more of these minerals could be used as a pathfinder for tin. The results accruing from this work exceeded our expectations. We now know that gold, galena, tetrahedrite, and particularly sphalerite may be used as pathfinders for tin. The authors may be permitted to express a pardonable pride in the fact that, partly as a result of this work, the Canadian Geological Survey assisted in uncovering what is, to the best of the authors' knowledge, the most promising tin occurrence yet known in Canada.

This tin discovery is being described elsewhere, however, and this paper deals chiefly with the results obtained by analyzing spectroscopically one hundred and twenty-two Western Canadian and forty-two outside sphalerites and comparing and contrasting these results and conclusions with those ar-

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rived at by other workers, and drawing therefrom some deductions as to the relative importance of metallogenetic provinces on the one hand, and type of deposit on the other in controling the minor element content of sphalerite specimens taken from different localities. The question as to whether Western Canada as a whole has a characteristic minor element assemblage is examined, and a preliminary investigation is made of the differences occurring in some of the more important mining districts in British Columbia and the Yukon.

In addition to the elements listed in Table 2, other workers have reported cobalt, nickel, thallium, thorium, molybdenum, mercury, chromium, and palladium. However, these elements are somewhat rare, and their occurrence in sphalerite has not been investigated by the authors.

There has been one unexpected and possibly important by-product of this investigation. The authors have noted that there is a remarkably close correlation between the Western Canadian gold and silver deposits which have played out at relatively shallow depths and those deposits in 'which the manganese content of the associated sphalerite is relatively high. More detailed work will have to be done before any final conclusions are possible, but the evidence at hand does suggest that when gold and (or) silver are found associated with a sphalerite which is high in manganese, that gold and (or) silver deposit is not likely to persist to more than a thousand or perhaps fifteen hundred feet in depth.

<div align="center">PROCEDURE.</div>

The material for analysis consisted of the cleanest possible selected cleavage fragments of sphalerite. Approximately 20 milligram samples were placed in the lower or positive graphite electrode. Arc spectra of the sphalerite were recorded on Eastman Type II F (Tropical) plates which have a useful range from 2200 to 6800 A., using a Hilger medium quartz spectrograph.

Throughout the experiments, 110-volt direct current at 6 amperes was used, with a 2-mm. gap. The light source was focused at infinity and a slit width of 0.01 mm. maintained.

Each analysis consisted of a series of exactly tangent narrow strips, 2 mm. in width, comprising the successive spectra from top to bottom of: (1) the empty electrodes, (2) a wave-length scale, (3) the iron arc from Hilger's "Specpure" iron rods, (4) the sphalerite sample arced for 40 seconds (beyond the first 20 seconds), (5) the sphalerite sample arced for 20 seconds, and (6) the tin arc from C.P. tin.

For quantitative estimates on indium and tin, sphalerite known to be free from these elements was medicated with various known percentages of each, and the lines compared. Cadmium estimates were made by comparing the strength of the cadmium lines of the sample with the same lines of several samples which were wet assayed for cadmium. Gallium, indium, and germanium lines were compared with lines from spectra of Hilger's ratio powders containing these and other elements in known percentages in a zinc base. All other estimates, except vanadium, titanium, and tellurium were

based on the strength of the lines of sphalerites assayed for the elements in question. Where iron assays over three per cent are given, the sphalerite was suspected of being the marmatite variety and was wet assayed.

Whenever necessary, a standard plate of any particular element looked for was compared with the sphalerite sample by means of a Judd Lewis comparator, thus eliminating all uncertainties of wavelength and line identification.

Table No. 1 lists the lines which were found to be most satisfactory for our purposes.

TABLE 1.

Element	Lines Used for Determinations		
Antimony	2311.47,	2598.06,	3267.50
Arsenic	2349.84,	2780.19,	2860.45
Bismuth	2897.97,	3067.71,	
Cadmium	2288.01,	3261.05,	3403.65
Copper	3247.54,	3273.96,	
Gallium	2874.24,	2943.63,	4172.05
Germanium	3039.06,	3269.49,	
Gold	2427.95,	2675.95,	
Indium	3039.35,	3256.09,	4511.32
Iron	3020.49,	3020.64,	3021.07
Lead	2833.07,	3683.47,	4057.82
Manganese	2576.10,	4030.75,	4033.07
Silver	3280.68,	3382.89,	5209.06
Tellurium	2383.25,	2385.76,	
Tin	2839.99,	2863.32,	3175.02
Titanium	3349.03,	3361.21,	3653.49
Vanadium	3183.98,	3185.39,	4379.23
Zinc	3345.02,	3302.58,	3282.33

DISCUSSION OF RESULTS.

In this work the following elements were studied: cadmium, gallium, germanium, vanadium, titanium, manganese, iron, arsenic, indium, tin, copper, antimony, silver, lead, bismuth, tellurium, and gold. Cobalt, nickel, mercury, thallium, molybdenum, chromium, palladium, sodium, potassium, calcium, and lithium have not been considered in the present study.

On the basis of our own polished section studies and of the conclusions arrived at by other workers, we consider that the following elements are chemically combined with the sphalerite: cadmium, gallium, germanium, indium, manganese, and iron. On the other hand, the presence of arsenic, antimony, tin, copper, bismuth, tellurium, gold, silver, and lead are probably the result of one or more minerals containing these elements being mechanically included in the sphalerite.

The authors have no direct evidence to suggest the manner in which either the titanium or the vanadium occurs in the sphalerite. A chemical association is suggested by the fact that no vanadium or titanium mineral has yet been recognized in any of the many sphalerites which have been examined. However, it is possible that more detailed studies of thin and polished sections of sphalerite may reveal the presence of either titanium or vanadium minerals, or both.

We will deal with each of these elements in turn.

TABLE 2.

MINOR ELEMENTS IN WESTERN CANADIAN AND OTHER SPHALERITES.

	Cd	Ga	Ge	V	Ti	Mn	Fe	As	In	Sn	Cu	Sb	Ag	Pb	Bi	Te	Au
Golden Mining Division																	
1. Kicking Horse, B. C...L	.20		Tr	Tr	Tr	S				Tr	W		Tr	Tr			
2. Monarch, B. C......L	.20				Tr	Tr	M			Tr	W		Tr	Tr			
3. Paradise, B. C....L	.40	Tr		Tr	Tr	Tr	S		M	.10	M	Tr	W	S			
4. Silver King, B. C....L	.40			Tr	Tr	Tr	S			Tr	Tr		Tr	Tr			
Fort Steele Mining Division																	
5. Sullivan, B. C.......H	.40	Tr		Tr	Tr	S	9.90			Tr	Tr	W	W	Tr	S		
Revelstoke Mining Division																	
10. Allco, B. C..........M	.40					Tr	S			Tr		W		Tr	Tr		
Lardeau Mining Division																	
15. Lead Star, B. C......M	.40					Tr	S		Tr	Tr	M		Tr	M			
16. Excise, B. C.........M	.30						M				Tr		Tr	Tr			
17. Mohawk, B. C........M	.40						S		Tr		Tr		Tr	Tr			
18. Elsmere, B. C........M	.40				Tr		S				S		Tr	S			
19. True Fissure, B. C....M	.40				Tr		S		Tr	.05	S		Tr	Tr			
20. Broadview, B. C......M	.40				Tr		S			.05	S		W	S			
21. Ajax, B. C...........M	.40				Tr		S		Tr		M	Tr	Tr	Tr			
22. Abbot, B. C..........M	.40					W	S	Tr			M		Tr	W			
23. Silver Cup, B. C.....M	.40				Tr		S			.10	S		W	W			
24. Hercules, B. C.......M	.40				Tr		S		Tr	.05	M		W	S			
25. Surprise, B. C........M	.40				Tr		S				M	Tr	W	S			
26. Lavina, B. C.........M	.40					M	S	Tr	Tr	.05	S		W	S			
Slocan Mining Division																	
30. Monitor, B. C........M	.40					W	S			Tr	M	W	W	Tr			
31. Payne, B. C..........M	.50					Tr	S			.10	M		W	Tr			
32. Lucky Jim, B. C......M	.40	Tr			Tr	W	3.36		Tr	.15	M		Tr	Tr			
33. Surprise, B. C........M	.40					W	M			.05	M	Tr	W	Tr			
34. Deadman, B. C.......M	.40					Tr	S			.15	M		W	Tr			
35. Noble Five, B. C.....M	.40				Tr	W	S	Tr		.15	M		Tr	Tr			
36. American Boy, B. C...M	.40					Tr	M			.15	M		W	Tr			
37. Silversmith, B. C.....M	.40					M	M			.15	S	Tr	S	Tr			
38. Ivanhoe, B. C........M	.50					Tr	S			.15	S		S	Tr			
39. Standard, B. C.......M	.40		Tr	Tr		W	S			.10	M		W	Tr			
40. Mammoth, B. C......M	.40					W	M			.10	M	Tr	W	Tr			
41. Bosun, B. C..........M	.40					Tr	M			.15	M	M	M				
42. Hewitt, B. C.........M	.40	W				W	S	Tr		Tr	S	S	S	S			
43. Van Roi, B. C.......M	.50	Tr					M			.10	M	W	M	Tr			
44. Enterprise, B. C......M	.40					Tr	S			Tr	W		W	W			
45. Two Friends, B. C....M	.40			Tr	Tr	Tr	W			Tr	W		W	Tr			
46. Black Prince, B. C....M	.40				Tr	Tr	M			Tr	W		W	Tr			+
47. Bank of England, B. C.....M	.50				Tr		W			Tr	Tr		W	Tr			+
48. Waterloo, B. C.......M	.50	Tr				M	S	Tr		Tr	S	Tr	M	M			+
Ainsworth Mining Division																	
59. Charleston, B. C......M	.40						M			Tr	M	Tr	Tr	Tr			
60. Whitewater, B. C.....M	.40					W	S		Tr	.20	M	Tr	Tr	W			
61. Boon, B. C...........M	.40					W	M			.10	M	Tr	W	W			
62. Winona, B. C.........M	.50						M			.15	M	Tr	W	S			

1. Figures in percent
2. S— + 0.5%
3. M— + 0.1-0.5%
4. W— +0.01-0.10%
5. Tr— − 0.01%
6. +—Present.
L—Low Temperature
M—Intermediate Temperature
H—High Temperature.

Note: Breaks in spacing indicate that mines are not in close proximity.

Ainsworth
63. Jac...
64. Boa...
65. Cor...
66. Silv...
67. Blu...

Nelson M...
73. Silv...
74. Cal...
75. Goo...
76. Ym...
   E...
77. We...

78. Hov...
79. Ren...
80. Koo...
81. Que...
82. Bay...

83. Fru...

Greenwoo...
90. Hig...
91. Car...
92. Pro...
93. Aet...

Vernon M...
100. Mo...
101. St...

Osoyoos...
105. Fai...

Similkam...
110. Tul...

Nicola M...
115. Ent...
116. Alm...
117. The...

Kamloo...
120. Cot...

Ashcroft M...
125. Roc...
   V...

Lillooet...
130. Hur...
131. Rob...
132. Min...

TABLE 2.—*Continued.*

	Cd	Ga	Ge	V	Ti	Mn	Fe	As	In	Sn	Cu	Sb	Ag	Pb	Bi	Te	Au
Intensity of Elements Present																	
Ainsworth Mining Division																	
63. Jackson Basin, B. C...M	.50	Tr				Tr	5.84		W	.30	S		M	W			
64. Boadicea, B. C......M	.40					Tr	S			Tr	M	W	W	M			
65. Cork Province, B. C...M	.40	Tr				Tr	S			.10	S		W	W			
66. Silver Hoard, B. C....M	.40				Tr		S				M	S	M	S			
67. Blue Bird, B. C......M	.40					Tr	S		Tr	.05	S		Tr	Tr			
Nelson Mining Division																	
73. Silver Leaf, B. C...M	.40				Tr	Tr	S		Tr		M		Tr	W			
74. California, B. C...M	.70					W	S	Tr		Tr	W		W	M			
75. Goodenough, B. C....M	.90			Tr	Tr	W	S		Tr	Tr	W	Tr	W	S			+
76. Ymir Yankee Girl, B. C.............M	.90			Tr	Tr	W	S		W	Tr	M	Tr	W	S			+
77. Wesko, B. C........M	.50			Tr	Tr	W	S			Tr	W	Tr	W	S			+
78. Howard, B. C.........M	.60					W	S			.05	M		Tr	W			+
79. Reno, B. C...........M	.40				Tr	W	S				W		Tr	S			
80. Kootenay Belle, B. C..M	.40			Tr	Tr	Tr	S		M	.05	M		Tr	M			
81. Queen, B. C..........M	.30				Tr	Tr	M		W		Tr		Tr	M			
82. Bayonne, B. C........M	.40			Tr	Tr	W	S		M		W		W	S			
83. Fruitvale, B. C......M	.50			Tr	Tr	W	S				M	Tr	M	S			
Greenwood Mining Division																	
90. Highland Bell.......M	.55					M	3.32				M	M	S	S			
91. Camp McKinney.....M	.75					W	S			.01	M	Tr	M	S			
92. Providence..........M	.90					W	S	Tr		Tr	M	Tr	M	M			
93. Aetna...............M	.60				Tr	M	S	Tr	W		S		M	M			
Vernon Mining Division																	
100. Mohawk............M	.90			Tr	Tr	Tr	S		Tr	.10	M	Tr	W	S			
101. St. Paul...........M	.80			Tr	Tr	Tr	M			.05	W	Tr	W	M			+
Osoyoos Mining Division																	
105. Fairview...........M	.75					Tr	M			Tr	M		W	W			
Similkameen Mining Division																	
110. Tulameen..........M	.30			Tr	Tr	Tr	S			.02	W						
Nicola Mining Division																	
115. Enterprise.........M	.50				Tr	Tr	S				S		W	S			
116. Almeda............M	.75				Tr	Tr	M		Tr		S			Tr			
117. Thelma............M	.40			Tr	W	Tr	S	W		Tr	S	S	M	S			
Kamloops Mining Division																	
120. Cotton Belt.........M	.20				Tr		S	M		.05	S	S	S	W	Tr		
Ashcroft Mining Division																	
125. Rocky Point, Walhachin, B. C....M	.30					M	S				M		W	Tr			
Lillooet Mining Division																	
130. Hurley River, B. C...M	.50					Tr	S		Tr	Tr	M		Tr	S			
131. Robson Group, B. C..M	.60	Tr			Tr	W	S	Tr	W	Tr	M	S	W	S			
132. Minto, B. C.........M	.50					M	S	Tr	Tr	Tr	S	Tr	Tr	Tr			

TABLE 2.—*Continued.*

						Intensity of Elements Present											
	Cd	Ga	Ge	V	Ti	Mn	Fe	As	In	Sn	Cu	Sb	Ag	Pb	Bi	Te	Au
New Westminster Mining Division																	
135. Brookmere, B. C......M	.50			Tr	Tr	W	S		M	Tr	S		W	M			
136. Allison Pass, B. C.....M	.50					W	S		Tr		W		Tr	Tr			
137. Skagit River Dev. Co..M	.40	Tr			Tt	M	S	W	M	.10	W S	M	M	W W	Tr		
138. Skagit River, B. C....M	.60	Tr			Tr	Tr	S		Tr	.10	M		Tr	W			
Vancouver Mining Division																	
145. Hell's Angels Claim, B. C.............M	.60			Tr	Tr	W	S				S		Tr	M			
146. Britannia No. 5, B. C..M	.30				Tr	Tr	S				S		M	S			
147. Britannia No. 8, B. C..M	.30				Tr	W	S		Tr		S		Tr	Tr			+
148. Britannia No. 8A, B. C...........M	.40				Tr	W	S		Tr	Tr	S		Tr	M			+
149. Britannia No. 8B, B. C............M	.30	Tr				W	S				S		M	S	Tr		
150. Britannia, B. C. (crystal)...........M	.20				Tr		W				Tr		Tr	M			
151. Lynn Creek, B. C.....M	.20					W	S				Tr			Tr			
Alberni Mining Division																	
154. W. W. W., B. C......H	.30				Tr	W	S				S		Tr	S			
Clayoquot Mining Division																	
155. Musketeer, B. C......H	.60				Tr	W	S			Tr	W		Tr	W			
156. Danzig, B. C........H	.30				Tr	M	S				Tr		Tr	Tr	W	Tr	
157. Mandalay, B. C......H	.50				Tr	M	S	Tr			S		Tr	W	Tr		
158. Privateer, B. C......H	.50				Tr	M	S	S		Tr	M		W	W			+
159. White Star Zeballos, B. C......H	.40				Tr	S		M			M		Tr	Tr			
160. Peerless, B. C......H	.40				Tr	W	S	W	W	Tr	S	Tr	W	S			+
161. Rey Oro, B. C.......H	.40				Tr	W	S	Tr		Tr	W	Tr	Tr	W			
162. Nimpkish Lake, B. C..H	.20				Tr	M	S				Tr		Tr				
163. June Group, B. C.....H	.50					M	S	Tr	M		M		W	Tr			
164. Pay Streak, B. C.....H	.40					M	S	Tr			S M		Tr	Tr			
165. Quatsino, B. C.......H	.20					W	S			Tr	M		Tr	Tr	M	W	
Cariboo Mining Division																	
175. Cariboo Gold Quartz, B. C.............M	.40				Tr		S		Tr	Tr	M		Tr	Tr	M		
176. Island Mountain, B. C............M	.55				Tr	Tr	S		Tr	.05	M		Tr	Tr			
177. Cariboo Hudson, B. C. M	.40						S			Tr	M		Tr	Tr			
Skeena Mining Division																	
185. Atlas Group, Burke Channel, B. C......M	.55	Tr			Tr	M	S				W		Tr	Tr			
186. Dominion Claim, Copper River, B. C..M	.55					M	S		W		M		Tr	Tr			
Omineca Mining Division																	
195. New Hazelton, B. C...M	.50				Tr		W				Tr		Tr	Tr			
196. Comet Group, B. C...M	.50				Tr		W				Tr	Tr	Tr	Tr			
197. Silver Standard, B. C..M	.75				Tr		W				Tr		Tr	Tr	W	M	
198. Silver Cup, B. C......M	.60				Tr		M				M	M	W	M			
199. Sunrise, B. C........M	.60				Tr		M			Tr	Tr	Tr	Tr	Tr			
200. Babine Bonanza, B. C. M	.60						1.66				S		M	M	S		

TABLE 2.—*Continued.*

	Intensity of Elements Present																
	Cd	Ga	Ge	V	Ti	Mn	Fe	As	In	Sn	Cu	Sb	Ag	Pb	Bi	Te	Au
Omineca Mining Division																	
201. Glacier Gulch, B. C....M|	.50				Tr		W				W		Tr	Tr			
202. Coronado, B. C......M	.40				Tr	M	M				M		Tr	Tr			·
203. Mamie, B. C.........M	.40				Tr	M	M				M		Tr				
204. Duthie, B. C..........M	.40				Tr	W	S			Tr	W	Tr	M	M			
Portland Canal Mining Division																	
205. Unuk River, B. C....M	.20					W	W				Tr		Tr	Tr			
206. Premier, B. C.......L	.20				Tr	W	M			Tr	M		Tr	Tr			
207. Marmot River, B. C. . M	.50					M	S		Tr		M		W	W			+
Atlin Mining Division																	
215. Atlin Ruffner, B. C....M	.75				Tr	M	S	W	Tr	.05	S		W	S			
Wheaton District, Yukon Territory																	
220. Porter Claim, Carbon Hill, Y. T..........M	.40				Tr		M				M	M	M	W			+
Mayo District, Yukon Territory																	
225. Elsa, Galena Hill, Y. T...............M	.30						M			.05	W		Tr	W			
226. Lake Group, Keno Hill, Y. T...........M	.50				Tr		S ·		Tr	Tr	W	W	M	S	W		
227. Lucky Queen, Keno Hill, Y. T..........M	.40				Tr	Tr	S	Tr		.05	S	S	S	Tr			
228. Keno, Keno Hill, Y. T. M	.50				Tr	Tr	S			Tr	Tr		W	Tr			
229. Hope, Keno Hill, Y. T. M	.50				Tr	Tr	M			.10	M	Tr	W	Tr	·		+
Yellowknife, Northwest Territories																	
250. Con Mine, N. W. T...L	.40					Tr	S	Tr	Tr	Tr	S	S	S	S	Tr		+
Manitoba																	
Flin Flon.............H	.30	Tr	W			Tr	S	Tr		.	S	M	M	S			+
Ontario																	
Albemarle...........L	.20						M				Tr						
Frontenac...........L	20					M	S			Tr	W		Tr	M			
Quebec																	
Calumet Island.......H	.20					M	S				W	Tr	W	S			
Cascapedia..........M	.20				Tr	Tr	M				Tr		Tr	Tr			
Newfoundland																	
Spider Pond.........L	.30	Tr	Tr			Tr	S			.02	W		W	W			
Montana																	
Emma Mine, Butte...M	.20				Tr	W	S		Tr		W		Tr				
Rainbow Vein, Butte..M	.20	W	Tr			W	M	Tr	W		M		Tr	W			
Superior Vein, Butte..M	.20				Tr	W	M			Tr	M		Tr	W			
Colorado																	
Georgetown, Clear Creek.............M	.40	Tr	M				S		Tr	Tr	Tr	Tr	M	Tr	Tr		
Kokomo.............M	.40	Tr				Tr	W	S		Tr	Tr	W		Tr			

TABLE 2.—Continued.

	Cd	Ga	Ge	V	Ti	Mn	Fe	As	In	Sn	Cu	Sb	Ag	Pb	Bi	Te	Au
Utah																	
Beaver County																	
(Triboluminescent) .M	1.0	W	W	Tr	Tr	W	S	Tr		Tr	W	Tr	W	S			
Silver King Coalition .M	.50	W	Tr			M	0.09	W	Tr	.05	S	W	M	S			
Arizona																	
Montana Mine, Ruby .M	.60			Tr	Tr	M	0.53	Tr		Tr	S	S	M	M			
Mexico																	
Cananea .M	.40	Tr		Tr	Tr	W	0.47		.10		M	Tr	W	S			
Sonora .M	.40					Tr	M				W		Tr	W			
Missouri																	
Joplin .L	.40	Tr	Tr				M				M		W	Tr			
Joplin (Ruby blende) .L	.40	W	M				W				M		Tr	W			
New York																	
Edwards .H	.40	Tr	Tr	Tr	Tr	W	S				Tr		Tr	Tr			
Pennsylvania																	
Friedensville .L	.20	W		Tr	Tr	Tr	M				W		Tr	Tr			
Phoenixville .L	.30	Tr	W	Tr	Tr		S				Tr		Tr	Tr			
Greenland																	
Ivigtut .H	.30	Tr			Tr	W	S		W	.02	S		W	W			
England																	
Cornwall .H	.40	Tr				W	M			Tr	W	W	Tr	M			
Castleton, Derbyshire .L	.60	Tr	W	Tr	Tr	M	M				M	Tr	Tr	Tr			
Frizington, Cumberland .L	.40				Tr		S				Tr		Tr	W			
Neuthead, Cumberland .L	.40	Tr	W				S			.02	M		Tr	Tr			
Spain																	
San Traganton .M	.40	W	W	Tr	Tr	Tr	S	Tr	Tr	Tr	S	Tr	W	W			
France																	
Arrens .M	.20						M				Tr		Tr	Tr			
Pierrefitte .H	.40	Tr	Tr		Tr	Tr	S	Tr		.10	W		Tr	Tr			
Valle d'Argele .M	.40	Tr	W			W	S				W		Tr	Tr			
Villemagne .M	.40	Tr	Tr		Tr	Tr	S		W	Tr	M	Tr	W	W			
Germany																	
Aachen .L	.30		Tr		Tr	Tr					W		Tr				
St. Christophe .M	.30				Tr	Tr	S	11.7		Tr	.15	W	W	Tr	Tr		
Ems, Hesse-Nassau .L	.30					Tr	W						Tr	Tr			
Neudorf-Harz .M	.40			Tr	Tr	Tr	S	W		Tr	Tr	M	Tr	Tr	S		
Westphalia .L	.40	Tr	Tr			S	S			.10	M	M	Tr	W	M		+
Hungary																	
Kapnik .L	.50					M	S			Tr	W		Tr	Tr			
Rodna .L	.40					M	10.6		Tr		M		Tr	Tr			+
Schemnitz .L	.30			Tr	Tr		M				W		Tr	Tr			
Australia																	
Broken Hill, N. S. W. .H	.20				Tr	S	S				Tr	Tr	Tr				
Broken Hill, N. S. W. .H	.20					S	8.58			.05	M		Tr				
Broken Hill, N. S. W. .H	.20				Tr	S	S				Tr		Tr	W			

A. Elements Chemically Combined with Sphalerite.

Cadmium. It is generally believed that where the presence of the cadmium sulphide greenockite is not detected, cadmium is present in sphalerite in solid solution. From a comparison of the lattice parameters [2] of CdS and ZnS, it may be seen how isomorphism is readily possible.

Compound	Structure	Lattice Parameter	Atomic Diameter
ZnS	Diamond	5.43A	2.35A
CdS	Diamond	5.82A	2.53A

There appears to be no general agreement regarding the physico-chemical conditions governing the concentration of cadmium in sphalerite. Graton and Harcourt [3] state that cadmium is rarely fixed under orthotectic conditions, and that it tends to avoid the more intense phases of hydrothermal deposition. Their results, based partly on a limited number of samples of sphalerite, show the cadmium content increasing with the decreasing intensity character of the deposits.

Stoiber,[4] however, believes that low temperature sphalerite from other than epithermal veins rarely contains over 0.6 per cent cadmium, and that cadmium concentration in sphalerite from intermediate and high temperature deposits varies from 0.01 to over one per cent. He concludes that high concentrations of cadmium would seem likely to occur in sphalerite from deposits of other than low temperature type.

According to Traill,[5] sphalerite from the Mill Close Mine in Derbyshire, which may be classed as a low temperature type of deposit, contains a valuable one per cent cadmium. On the other hand, a sphalerite from a high intensity type deposit at Bottino, Tuscany, contains 1.23 per cent cadmium.[6]

Hintze [7] records that the cadmium content appears to be higher in wurtzites than in sphalerites. Our highest cadmium content was obtained from a triboluminescent sphalerite with wurtzite, from Beaver County, Utah. Excluding this sample, we obtained highest cadmium in sphalerite from mesothermal deposits, and least cadmium from high temperature types of deposits. On the whole, our results show that cadmium concentrations are highest in intermediate temperature types and lowest in hypothermal and pyrometasomatic types of deposits.

A consideration of Table 2 shows, however, that although there is a tendency for sphalerite in mesothermal deposits to carry relatively high concentrations of cadmium, there is little doubt but that the controlling factor is the availability of cadmium in the ore-bearing solutions of a particular

[2] Wyckoff, R. W. G.: The Structure of Crystals, A.S.C. Series, No. 19, 1931.

[3] Gratin, L. C., and Harcourt, G. A.: Spectrographic evidence on origin of ores of Mississippi Valley type. Econ. Geol. 30: 812, 1935.

[4] Stoiber, R. E.: Minor elements in sphalerite. Econ. Geol. 35: 513, 1940.

[5] Thraill, J. G.: The geology and development of Mill Close Mine, Derbyshire. Econ. Geol. 34: 883, 1939.

[6] Stoiber, R. E.: op. cit., p. 513.

[7] Graton, L. C., and Harcourt, G. A.: op. cit., p. 812.

district. Sphalerite from the Golden Mining Division consistently carries less cadmium than does sphalerite from the Ymir or Greenwood Mining Divisions; all the deposits of the latter Divisions are of a medium temperature type.

Furthermore, the samples of sphalerite from Manitoba, Ontario, Quebec, and Newfoundland are all relatively low in cadmium, and yet they come from deposits classified as high, medium, and low temperature types.

It is interesting to observe that the average cadmium content of the 122 Western Canadian sphalerites analyzed is close to 0.45 per cent, and that that of the ten sphalerites from the Western United States and Mexico is 0.43 per cent. In contrast, sphalerites from Eastern Canada, Newfoundland, Greenland, and the Eastern United States average less than 0.30 per cent. On somewhat scanty evidence it appears that England, the Tri-State District, and Hungary are also areas of relatively high cadmium-bearing sphalerites, whereas sphalerites from France, Germany, Spain, and Australia are relatively low in cadmium.

In general, it may be said that Western Canada, which is a part of the Cordillerean section of North America, is in a metallogenetic province which is relatively high in cadmium.

Gallium. This element occurs in a number of minerals in spectrographic amounts. Spectrographic research has shown it to be of common occurrence in sphalerite and a number of other minerals, chiefly the aluminous silicates.

The close relation of gallium to aluminium in the periodic table is confirmed by the intimate natural association of gallium to aluminous minerals and rocks.[8] From findings of Goldschmidt and Peters[9] it appears that the gallium content increases in the course of rock differentiation from ultrabasic to acidic and alkalic phases, which likewise corresponds in a general way to rising aluminium content; the increase in gallium continues notable in the pegmatites, and especially in those approaching hydrothermal characteristics. The finding by Papish and Stilson[10] of gallium in all specimens of gahnite examined indicates a two-fold allegiance of the element to aluminium and to zinc. Papish's finding of noteworthy gallium in lepidolite is in line with the conclusions of Goldschmidt and Peters just mentioned. We obtained similar results on gahnite and lepidolite. Goldschmidt and Peters showed that the sphalerite of the Ivigtut occurrence carries much more gallium than the aluminium-rich cryolite of the same occurrence. We also obtained similar results on this material.

Graton and Harcourt say the general available data suggest that gallium tends to concentrate with aluminium from the earliest stages of magmatic differentiation until those stages are reached where sulphide deposition appears, and that thereafter the gallium tends to desert such aluminium minerals as are then formed in favour of ZnS.

In the body-centered cubic, face-centered cubic, and diamond type of structures, if "a" is the length of the unit cell, the closest approach of the atoms (atomic diameter) is given by the expressions:

8, 9, 10 Graton, L. C., and Harcourt, G. A.: op. cit., pp. 813–814.

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Body-centered cube..............................866a
Face-centered cube.............................707a
Diamond type...................................434a.
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The hypothesis has been put forward by Hume-Rothery [11] and others, that where the atomic diameters of solute and solvent differ by more than about 15 per cent of that of the solvent, the "size-factor" is unfavorable, and the solid solution is very restricted; when the atomic diameters are within this limit the size factor is favorable, and considerable solid solutions may be formed.

The possibility exists that gallium may be present in sphalerite as (1) GaAs, (2) GaSb, (3) GaP, (4) GaS, and (5) as an atomic dispersion of gallium (to a small extent only). The first three compounds all have the same structural arrangement as sphalerite, and closely similar lattice dimensions.[12]

Compound	Structure	Length of Unit Cell			Atomic Diameter
		a	*b*	*c*	
ZnS	Diamond	5.43A			2.35
GaAs	Diamond	5.63			2.44
GaSb	Diamond	6.11			2.65
GaP	Diamond	5.43			2.35
Ga	Orthorhombic	4.51	4.516	7.644	2.43–2.79

To account for the preference of gallium for sphalerite rather than for other sulphides, Goldschmidt and Peters [13] make the interesting suggestion that the element occurs as GaAs, which has the same structural arrangement as sphalerite. The authors, however, do not believe that gallium is present as GaAs, or as GaSb, because, of 33 gallium-bearing sphalerites which were examined, only nine showed the presence of arsenic, and 15 the presence of antimony. It is interesting to note that all the antimony-bearing sphalerites also contain lead and copper, indicating the presence of one of the lead antimonides, tetrahedrite, or both.

The spectral lines 4172.0, 4033.0, and 2943.0 are commonly used to establish the identity of gallium. Under the conditions existing in this work, the line 4033.0 is overlapped by spectral lines of manganese and iron, and was not used. As graphite electrodes were used in the production of the arc, the line at 4172.0 was determined with difficulty in some cases, due to the interference of cyanogen bands. If this line is of low intensity, it may be obscured by the cyanogen band, and as a result the authors believe that minute traces of gallium in some of the sphalerites examined were not detected.

The work of Graton and Harcourt, Stoiber, and Papish and Stilson all shows that the higher temperature occurrences of sphalerite contain less gallium than those of lower-intensity origin.

11 Hume-Rothery, W.: Structure of Metals and Alloys. Inst. of Metals, 1936. P. 30.
12 Wyckoff, W. R. G.: op. cit., 1931.
13 Graton, L. C., and Harcourt, G. A.: op. cit., p. 815.

As only eleven sphalerites from Western Canada were found to contain gallium, we hesitate to draw any general conclusions; but on the basis of this limited number, our results show agreement with prior findings that the gallium content of sphalerite increases with declining intensity character of the deposits.

Western Canada, as a metallogenetic province, appears to be low in gallium.

Germanium. Germanium appears to be quite rare in sphalerite from Western Canada. As only two samples were found to contain germanium, we decided to test the sensitivity of our spectrograph by analyzing a number of minerals reported by Papish [14] to contain germanium, as well as a number of foreign sphalerites.

Papish found traces of germanium in enargite, sphalerite, topaz, tourmaline, spodumene, and lepidolite. We obtained similar results and, furthermore, checked very well with Stoiber in finding germanium in numerous foreign sphalerites. We also noted the presence of germanium in a specimen of colusite from Butte, Montana.

In the tin ores of Bolivia, Moritz [15] found that germanium in the solutions is enriched only at very low temperatures.

Goldschmidt and Peters [13] conclude that hydrothermal sphalerite are richer in germanium than those of pyrometasomatic origin. They also find that sphalerite and wurtzite of lower-intensity conditions of formation have higher germanium content than those of deeper hydrothermal zones. The results of our foreign sphalerite analyses are in agreement with the above findings.

As the Consolidated Mining and Smelting Company of Canada, Limited, are by far the largest producers of zinc in British Columbia, we asked them to examine our report. They reported that the results presented agree fairly well with their data, but added that "We have found that germanium is much more common than is indicated in this report. Very few of the concentrates tested here have been germanium-free. This element is present, usually, in such minute amounts that detection by direct spectroscopic methods is unlikely. Our determinations are made on a 'chemical concentrate' obtained by leaching."

As to the mode of occurrence of germanium in sphalerite, it may be present either as GeS, on which no information was available, or as an atomic dispersion of Ge. The latter would be readily possible, as the structure is similar and the size factor is well within the 15 per cent permissible.

Compound	Structure	Lattice Parameter	Atomic Diameter
ZnS	Diamond	5.43	2.35
Ge	Diamond	5.82	2.44

[14] Papish, J.: New occurrences of germanium. ECON. GEOL. 23: 660–670, 1928, and 24: 470–480, 1929.
[15] Ahlfeld, F.: The Bolivian Tin Belt. ECON. GEOL. 31: 57, 1936.

It is interesting to observe that the only two samples of British Columbia sphalerite which showed germanium came from two properties situated close to one another in the Slocan Mining Division. Similar results have been obtained by W. H. Matthews of the B. C. Department of Mines.[16]

Consequently, although germanium does occur in some Western Canadian sphalerites in amounts too small to be detected by the spectrographic methods we have employed, it is, nevertheless, relatively rare, and Western Canada as a metallogenetic province may be said to be low in germanium.

Indium. The occurrence of indium, the next heavier relative of gallium in the periodic table, is less well investigated than cadmium, gallium, and germanium.[17] No independent indium mineral is known. We check with Graton and Harcourt in finding it in ores of iron and manganese, of tin and tungsten, and in many sphalerites.

Graton and Harcourt quote Goldschmidt, Barth, and Lunge [18] as expressing the belief that indium probably occurs in sphalerite in the bivalent form. This seems to us highly improbable, as the structure of indium is the face-centered tetragonal type as compared to the diamond type for sphalerite, and the atomic diameter of indium exceeds the allowable 15 per cent. The compound InSb [19] has the same crystal structure as sphalerite, but the atomic diameter is 2.80, which exceeds the allowable 15 per cent; thus InSb may form only a very restricted solid solution with sphalerite.

The lines most easily determined under the conditions encountered in this work were 3256.03 and 3039.36. If these lines were absent, the lines 4511.32 and 4101.82 were absent or inconclusively identified because of interference sometimes caused by band heads of carbon.

Graton and Harcourt drew no conclusions as to the order of magnitude of indium in sphalerite, but Stoiber suggests that the concentration of indium is least in sphalerite from low temperature deposits, is greater in that from both high and intermediate temperature deposits, and is usually greatest in sphalerite from mesothermal deposits. Our results on indium show complete agreement with those of Stoiber.

Nevertheless, if Table 2 is studied, it can readily be seen that the area, rather than the type of the deposit in which the sphalerite occurs, is the controlling feature. Sphalerite from the Lardeau and New Westminster Mining Divisions shows indium most consistently, but the Fort Steele, Revelstoke, Ainsworth, and Cariboo Divisions also show some.

Manganese. Manganese was found in every type of sphalerite and in a large majority of the sphalerite samples.

A study of Table 3 indicates clearly that the manganese content of sphalerite tends to be higher in the deposits which have been formed at high temperatures. This is in accord with the findings of other workers.

It may not be of significance, but it certainly is of interest to note that, of all the sphalerites which were examined, those which contained the most manganese came from the Sullivan Mine in British Columbia and from

16 Matthews, W. H.: Dept. of Mines, Victoria, B. C., personal communication.
17, 18 Graton, L. C., and Harcourt, G. A.: op. cit., p. 816.
19 Wyckoff, W. R. G.: op. cit., 1931.

Broken Hill in New South Wales, two of the great base metal mines of the world.

The atomic structure of manganese is complex, and as yet no suggestion has been made as to its mode of occurrence in sphalerite. Manganese and iron are frequently associated in minerals and, consequently, it is possible that manganese replaces isomorphously the iron which is found in sphalerite.

However, just as is the case with the preceding elements, the sphalerite from some areas contains significant amounts of manganese, whereas the sphalerite from other areas contains virtually none. Sphalerite from Western Canada usually contains manganese, but, nevertheless, some areas—notably that north of Hazleton and the Cariboo—are exceptionally low.

There may be some connection between the depth to which a gold or silver deposit may persist and the manganese content of an ore as revealed by the manganese content of the sphalerite in that ore. This will be discussed in a later portion of this paper.

Iron. The iron content of sphalerite is extremely variable. In general, the lighter the color of the sphalerite the less iron it contains. This generalization holds well in the case of yellow, red, light brown, and yellowish-green varieties of sphalerite, but is not necessarily true when dealing with the many shades of dark brown and black sphalerite. In general, the black varieties of sphalerite proved to be marmatite with an iron content ranging from eight to twelve per cent iron. However, by no means do all the dark brown and brownish-black varieties of sphalerite contain enough iron to be classified as marmatite. Indeed, many of the so-called marmatites from the Slocan contain less than four per cent iron, and some of this iron is definitely known to be contributed by admixed pyrite, chalcopyrite, stannite, and pyrrhotite.

Actually, the majority of the sphalerite samples examined contained more than 0.5 per cent iron, and it is possible that if quantitative analyses were available, some of these would prove to be marmatite. On the basis of our analyses, it seems that there are fewer marmatites in Western Canada than has previously been thought to be the case. The Sullivan mine does, however, contain marmatite. The evidence given above suggests that the high iron content of some of the zinc concentrates produced in British Columbia results from unsatisfactory milling rather than from unsolvable mineralogical problems.

B. Elements Mechanically Combined with Sphalerite.

Tin. On account of its possible economic significance, the occurrence of tin in sphalerite is of particular interest in British Columbia and the Yukon. Many of the sphalerites with a relatively high tin content were both mounted in bakelite and examined by reflected light, and crushed and superpanned. In most cases, stannite or cassiterite, or both, were found, both minerals being much more prevalent than was heretofore suspected.

Sphalerite is by no means the only tin carrier. Indeed, other minerals may be better indicators at a particular mine, as boulangerite and pyrrhotite

seem to be at the Sullivan. Gold, tetrahedrite, and galena all may carry tin, but sphalerite is more widespread in Western Canada than gold or tetrahedrite, and it tends to carry slightly higher and more uniform amounts of tin than does galena. Consequently, all in all, sphalerite may be said to be the best pathfinder in a preliminary search for tin.

Copper, Silver, Lead, Antimony, and Arsenic. All these elements are frequently found in British Columbia and the Yukon.

Examinations of numerous polished sections of sphalerite containing one or more of the above elements usually reveal the presence of one or more minerals composed of them, even when the sphalerite has been picked with the greatest possible care. Galena, tetrahedrite, pyrargyrite, polybasite, boulangerite, zinckenite, jamesonite, bournonite, chalcopyrite, native silver, and arsenopyrite have all been found intimately mixed with sphalerite from one or more localities. There is, therefore, no reason to postulate a chemical relationship between any of the above elements and sphalerite.

Copper, like iron and cadmium, has been found in every sphalerite which has been examined. Silver and lead, although not similarly ubiquitous, are nearly so, and both were found in 119 out of the 122 samples of sphalerite from Western Canada. Silver and lead are nearly as common in the other sphalerite samples which have been examined, and are actually found in a higher percentage of samples than is manganese.

Antimony and arsenic were found in 38 and 19 per cent, respectively, of the Western Canadian samples. Antimony occurred somewhat less frequently—32 per cent—in the outside samples, but the figure for arsenic was virtually identical.

Gold, Bismuth, and Tellurium. Gold, bismuth, and tellurium are found in several localities in British Columbia. Curiously enough, in spite of the fact that tellurbismuth, tetradymite, and joseite have all been found closely associated with gold in British Columbia, nagyagite, the gold-bearing bismuth telluride, has until the present time never been found. Furthermore, the gold-bearing tellurides are rare and have never been observed associated with sphalerite.

It would be natural to suspect that nagyagite had been overlooked, but the results given in Table 2 do not support this supposition. Sixteen samples of sphalerite show gold, but not one of these contains tellurium, and only one, bismuth. On the basis of many polished sections, it seems probable that most, if not all, of the gold found in Western Canada sphalerite is present as minute inclusions of gold, electrum, or auriferous silver.

Tellurium, where present, is always accompanied by bismuth, and therefore it is probable that the presence of one of the bismuth tellurides may safely be inferred. Bismuth, however, is often found without tellurium, and in these cases the bismuth may be assumed to result from small amounts of native bismuth, bismuthinite, or one of the lead bismuthinites, all of these minerals having been recorded in various areas in British Columbia although they have not always been specifically determined in association with the particular samples of sphalerite dealt with in Table 2.

C. Elements Whose Mode of Occurrence is Doubtful.

Titanium. This element is found in every type of deposit and our results indicate no preference for any type of occurrence.

No titanium mineral has been found with any of the samples of sphalerite, but until a great number of thin sections have been made and studied, the absence of such a mineral as rutile may not be even inferred, much less assumed.

The authors have found titanium to be present in many minerals, and have observed, in one of these minerals inclusions, too small to identify satisfactorily. These minute inclusions may well be rutile. Rutilated quartz is occasionally noted, rutile is present in inconspicuous amounts in many rocks, and it is just possible that it is present in some sphalerites where it could be easily overlooked if only polished sections of the sample are studied.

Vanadium. Like titanium, this element is present in every kind of deposit, but it definitely shows a tendency to occur in deposits of the low-temperature type.

It is interesting to note that sphalerite often contains no vanadium, even though the vein carrying the sphalerite is traversing rocks in an area where vanadium is known to occur. The north end of Vancouver Island contains many dark colored lavas and these lavas, and particularly the femic minerals in these lavas, are known to contain traces of vanadium. Nevertheless, not one single sample of sphalerite from this area shows even a trace of vanadium.

In some districts vanadium is conspicuous only by its absence, but in other districts it occurs sporadically in the sphalerite. Insufficient work has been done to enable any opinion to be formed as to whether the occurrence of vanadium in the sphalerite of one mine is uniform.

On the basis of the work so far done, it may be said that vanadium is relatively rare in the sphalerite samples of Western Canada.

The results tabulated in Table 2 show clearly that the metallogenetic province or district is the factor which is most decisive in determining the presence or absence of vanadium in sphalerite. Tables 3 (a) and (b) between them indicate that, other things being equal, vanadium shows a decided preference for sphalerite when the sphalerite is associated with a deposit of a low-temperature type.

Taking into account all the evidence cited above, it seems probable that at least some of the vanadium in sphalerite has been introduced by surface solutions.

TYPE OF DEPOSIT FAVORED BY SOME OF THE MINOR ELEMENTS.

Tables 3 (a) and (b) show in a condensed form the concentration and distribution of cadmium, gallium, germanium, indium, tin, manganese, iron, gold, vanadium, and titanium in the sphalerite samples from Western Canada and from elsewhere.

At this point it must be stated again that, with the exception of cadmium, the figures are valuable more for purposes of comparison than they are for their absolute accuracy. In the case of cadmium, the availability of check

chemical analyses has shown that the results are quantitatively, as well as qualitatively dependable.

From Table 2 it is possible to draw the generalization that the factor which is of greatest importance in determining the minor element content of a sample of sphalerite is the metallogenetic province or district in which that sphalerite occurs. Similarly, from Table 3, it is possible to state that there is a tendency for some elements to favor a particular type of deposit.

Cadmium, iron, and copper occur in every sample of sphalerite which has been examined. Of these three elements, cadmium and iron have been in-

TABLE 3 (a).

MINOR ELEMENT DISTRIBUTION IN SPHALERITE FROM WESTERN CANADA.

Element	Concentration	Temperature Type of Deposit					
		High (13)		Medium (103)		Low (6)	
		No.	Per Cent	No.	Per Cent	No.	Per Cent
Cd	+.50%	1	8	22	21	0	0
	+.10-.50	12	92	81	79	6	100
Ga	<.01	1	8	9	9	1	17
	Nil	12	92	94	91	5	83
Ge	+.01-.10	0	0	1	1	0	0
	<.01	0	0	1	1	0	0
	Nil	13	100	101	98	6	100
In	+.10-.50	1	8	4	4	1	17
	+.01-.10	1	8	6	6	0	0
	<.01	2	15	25	24	1	17
	Nil	9	69	68	66	4	67
Sn	+.10-.50	0	0	10	10	0	0
	+.01-.10	0	0	27	26	1	17
	<.01	5	38	28	27	5	83
	Nil	8	62	38	37	0	0
Mn	+.50	1	8	0	0	0	0
	+.10-.50	6	46	14	14	0	0
	+.01-.10	5	38	30	29	1	17
	<.01	1	8	38	37	4	67
	Nil	0	0	21	20	1	17
Fe	+.50	13	100	73	71	3	50
	+.10-.50	0	0	22	21	3	50
	+.01-.10	0	0	8	8	0	0
	<.01	0	0	0	0	0	0
Au	Present	2	15	13	13	1	17
	Absent	11	85	90	87	5	83
V	<.01	1	8	14	14	3	50
	Nil	12	92	89	86	3	50
Ti	+.01-.10	0	0	1	1	0	0
	<.01	9	68	50	49	5	83
	Nil	4	32	52	50	1	17

TABLE 3 (b).

MINOR ELEMENT DISTRIBUTION IN OTHER SPHALERITES.

Element	Concentration	Temperature Type of Deposit					
		High (9)		Medium (17)		Low (16)	
		No.	Per Cent	No.	Per Cent	No.	Per Cent
Cd	+.50%	0	0	2	12	1	6
	+.10–.50	9	100	15	88	15	94
Ga	+.01–.10	0	0	4	24	2	12
	<.01	5	55	5	29	6	38
	Nil	4	45	8	47	8	50
Ge	+.10–.50	0	0	1	6	1	6
	+.01–.10	1	11	3	18	3	19
	<.01	2	22	3	18	4	25
	Nil	6	67	10	59	8	50
In	+.10–.50	0	0	0	0	0	0
	+.01–.10	1	11	3	18	0	0
	<.01	0	0	6	35	1	6
	Nil	8	89	8	47	15	94
Sn	+.10–.50	0	0	1	6	0	0
	+.01–.10	3	33	2	12	3	19
	<.01	2	23	8	47	2	12
	Nil	4	44	6	35	11	69
Mn	+.50	3	33	1	6	0	0
	+.10–.50	1	11	2	12	3	19
	+.01–.10	3	33	7	41	0	0
	<.01	2	23	5	29	4	25
	Nil	0	0	2	12	9	56
Fe	+.50	8	89	10	59	8	50
	+.10–.50	1	11	5	29	6	38
	+.01–.10	0	0	2	12	2	12
	<.01	0	0	0	0	0	0
Au	Present	1	11	0	0	2	13
	Nil	8	89	17	100	14	87
V	+.01–.10	0	0	0	0	0	0
	<.01	1	11	6	35	4	25
	Nil	8	89	11	65	12	75
Ti	+.01–.10	0	0	0	0	0	0
	<.01	5	55	11	65	6	38
	Nil	4	45	6	35	10	62

vestigated quantitatively. Table 3 reveals clearly that a high iron-bearing sphalerite is more apt to be found in a high, than in a low temperature type of deposit. On the contrary, high concentrations of cadmium are most likely to occur in moderate to low temperature types.

Gold and titanium show no marked preference in the type of deposit which they honor with their presence.

Manganese, like iron, favors high temperatures; but gallium, indium, and surprisingly enough, tin are most prominent in medium temperatures. Germanium and vanadium are most apt to occur in low temperature types of deposit.

Many anomalies may be found in connection with the above generalizations. However, virtually all may be explained by assuming or admitting the dominant importance of the metallogenetic province, or district, in determining the minor element content of a sample of sphalerite.

<div align="center">

COMPARATIVE FREQUENCY OF OCCURRENCE OF SOME OF THE
MINOR ELEMENTS IN SPHALERITE.

</div>

Cadmium, iron, and copper have been found in all the samples of sphalerite so far analyzed. The quantity of these elements present may vary widely in different samples. These are the "always present" minor elements and only their relative abundance is significant.

Silver, lead, and manganese have been found in more than three-quarters of the samples which have been studied. In general it may be said that, in a sample of sphalerite, their absence rather than their presence is a matter of interest. These are the "usually present" minor elements. They are to be found in seventy per cent or more of all the samples of sphalerite which have been examined. Occasionally their presence in relatively large or small amounts in a suite of samples is of interest.

Tin, titanium, indium, gallium, germanium, and antimony vary greatly in the frequency of their occurrence in sphalerite. In general, these elements may be expected to be found in from 25 to 75 per cent of all the samples of sphalerite which are analyzed. On the basis of Stoiber's [20] results, cobalt and nickel also belong in this group. These are the "often present" minor elements. These elements, unless consistently absent or consistently present in a suite of samples, are of minor interest.

Arsenic, vanadium, gold, bismuth, tellurium, and, on the basis of Stoiber's [20] investigations, thallium and molybdenum are all rare enough in their occurrence to be of interest if they are found. They appear in less than 25 per cent of the analyses of sphalerite and may be classed as the "occasionally present" minor elements.

MINOR ELEMENT CONTENT OF SPHALERITE FROM SOME SELECTED REGIONS.

On the basis of work done by Stoiber, by Graton and Harcourt, and by ourselves, it is now possible to make some generalizations of interest relative to a few mines and mining districts (Table 4).

MINOR ELEMENT CHARACTERISTICS OF SOME WESTERN CANADIAN DISTRICTS.

Western Canada, taken as a whole, is relatively high in tin and in gold, but is low in gallium, germanium, and vanadium. However, if this vast area is considered on the basis of smaller units, then a number of well-defined sub-divisions are clearly indicated. Lacking, for the present, more satis-

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[20] Stoiber, R. E.: op. cit., pp. 504–505.

TABLE 4.

(a)	L. Mississippi Valley Province,[1,2,3] U.S.A.	Present	Gallium and germanium
		Absent	Tin
(b)	H. Edwards, New York, [1,2,3] U.S.A.	Present	Gallium
		Absent or weak	Tin
(c)	L. Mississippi Valley Type[2,3] (Belgium, Poland, Germany)	Present	Germanium, thallium
		Absent	Gallium, tin, indium
(d)	L. Central Kentucky,[2] U.S.A.	Present	Gallium, germanium
		Absent	Manganese, tin
(e)	L. Cumberland,[1,2] England	Present	Nickel, cobalt, germanium
(f)	H. Cornwall,[1,2] England	Present	Tin
		Absent	Germanium
(g)	H. New South Wales,[1,2] Australia	Present	Cobalt, nickel, tin
		Absent	Gallium, germanium
			Also relatively high in manganese and low in cadmium.
(h)	L. Premier, B. C., [1,2] Canada	Absent	Gallium, germanium,[4] indium
(i)	H. Sullivan, B. C.,[1] Canada	Present	Gallium, indium, tin
		Absent	Germanium[4]
			Also relatively high in manganese.

[1] Basis of work by Warren and Thompson.
[2] Basis of work by Stoiber.[20]
[3] Basis of work by Graton and Harcourt.[21]
[4] It has already been stated that although no germanium has been found by spectrographic analyses of sphalerite, minute traces of this element may be present.
    H. Relatively high-temperature deposit.
    L. Relatively low-temperature deposit.

factory methods of classification, the Mining Divisions as indicated on the accompanying map, are used as a mean of reference.

The following table shows the average intensities of some of the more interesting minor elements present in sphalerite from these various Mining Divisions in British Columbia. A number of Divisions do not appear because sufficient samples were not available for analysis, and consequently, too few results were obtained for any satisfactory conclusions to be drawn (Table 5).

It is unsound to draw definite conclusions on the basis of only 122 samples of sphalerite which have been selected from such a vast area. However, a perusal of Table 2, in which the grouping of mines within a Mining Division is indicated by appropriate spacing between the properties or groups of properties, shows clearly that there is every probability that if sufficiently thorough and detailed work is carried on, every genetically related orebody will show a similar minor element content. Conversely, we may expect that it will be possible, on the basis of minor element content, to differentiate between two phases or periods of mineralization in one area.

To illustrate this point we may take samples 1 and 2 and contrast the cadmium content of these two closely related mines with that of 3 and 4, which are many miles distant and themselves are some miles apart. The analyses were made in a manner considered to remove all possibility of "wishful thinking." On the basis of these analyses, the suggestion is that

TABLE 5.

Mining Division	Average Intensity of Elements Present								
	Cd	Ga	Ge	In	Sn	As	Mn	V	Au
1. Golden	.3				Tr		Tr	Tr	
2. Fort Steele (Sullivan Mine)	.4	Tr		Tr	Tr		S	Tr	
3. Revelstoke	.4			Tr	Tr		Tr		
4. Lardeau	.4			W	Tr		Tr		
5. Slocan	.4				.10		Tr		
5(a). Slocan (Silverton Creek)	.4		Tr		W		Tr		
6. South Slocan	.4				Tr		Tr		
7. Ainsworth	.4			Tr	.10		Tr		
8. Nelson	.8				Tr		W	Tr	P
9. Greenwood	.7						W		
10. New Westminster	.5	Tr		W	Tr		W		
11. Clayoquot	.4					Tr	W		P
12. Cariboo	.5			Tr	Tr				
13. Omineca (except Hudson Bay Mtn.)	.6								
13(a). Hudson Bay Mountain	.4						W		
14. Mayo (Yukon)	.4				W		Tr		

Note: S .... Strong—+0.50%
W .... Weak —+0.01–0.10%.
Tr .... Trace — <0.01%
P .... Present
Figures are in per cent.

there are three different magmatic sources for these four properties, 1 and 2 having a common source; a surmise which, on the available geological information, seems to be in accord with the facts.

Another illustration, the facts of which have been corroborated independently [16] is that of samples 42 and 43. These two samples showed germanium, the only ones in Western Canada to do so. These two properties adjoin one another on Silverton Creek in the Slocan Mining Division. The B. C. Department of Mines [16] has analyzed every available sample of sphalerite from the Slocan, and has found germanium in only three; in the two samples 42 and 43 and in a sample from another nearby property from which the authors had no specimen.

The cadmium content of 145, when contrasted with that of 146–150, is conspicuous. All are in the same Mining Division, but sample 145 comes from a property 60 miles distant from where the other samples originated.

The example which interested the authors perhaps more than any other, was afforded by samples 195–199 inclusive, and 202–204 inclusive. The former contain nearly 50 per cent more cadmium and no manganese in contrast to the latter. On plotting the occurrences, it was discovered that the former all came from a small area north of Hazleton and the latter from Hudson Bay Mountain near the town of Smithers, the two areas being quite distinct geographically and, if the above minor element differences may be taken as a guide, quite distinct geologically.

The authors wish to make it quite clear that they are not claiming finality in any of these results, but they do believe that these results suggest the possibility that these minor elements may, by their distribution in sphalerite,

and in other minerals, afford geologists some assistance in studying the genesis of orebodies. Further detailed studies will be undertaken as soon as possible.

POSSIBLE RELATIONSHIP BETWEEN THE MANGANESE CONTENT OF AN ORE AND THE PERSISTENCE OF GOLD AND SILVER VALUES TO DEPTH.

British Columbia has had many gold and silver mines in which values have failed to carry to depth. Many mines have, after a promising start, come to a depressing end. In many instances, the vein persists, but the gold and silver values do not go below a thousand or perhaps fifteen hundred feet, and often much less, beneath the present surface.

The Cariboo and Bridge River Camps give promise of greater persistence and the former may well be counted on to possess veins which may persist in depth for several thousand feet.

Examining engineers have sought, so far largely in vain, for some simple method by which they might predict the depth to which—other factors being equal—native gold and (or) silver in a property might persist.

Dr. Malcolm Maclaren [22] as far back as 1908 drew attention to Lenher's experiments [23] in which it was shown "that gold is soluble in sulphuric, phosphoric, and other acids if a compound, as manganese di-oxide, capable of liberating oxygen be present." Maclaren noted that these experiments are of great importance as affecting the solution of gold in the upper portions of veins that lie within the reach of oxidizing waters.

All this was thought interesting, but apparently was considered only insofar as it affected secondary or supergene enrichment. In British Columbia there is much evidence that suggests that the depth to which these relatively shallow gold and silver deposits persist, is related to the topography of today.

In Table 6 there are listed one or more mines from most of the more important gold camps and a few of the silver properties in which native silver or other rich silver minerals are prominent. All these properties are in British Columbia and in the table are notes indicating the depth at which there is a marked decrease in the grade of the ore, usually of vital importance to the property, and the comparative amount of manganese present in the ore.

Of the 25 mines listed in Table 6, only five have so far been found to go to depths of well over fifteen hundred feet, and in every case these ores appear to have have little or no manganese present in their composition. In the camps which have been well bottomed, such as the Zeballos and Ymir, not only is there conspicuous sphalerite, but this sphalerite contains—relatively speaking—large amounts of manganese.

Much polished section work has been carried out, and it is interesting to note that the gold appears always to have been deposited after the sphalerite.

All the above suggests that, as the surface was approached by the ore-bearing solutions, conditions changed—probably by a decrease of temperature or pressure, or both, or by a mingling of vadose and plutonic solutions;

[21] Graton, L. C., and Harcourt, G. A.: op. cit., p. 803.
[22] MacLaren, M.: *Gold.* Min. Jour., London, 1908. P. 105.
[23] Jour. Amer. Chem. Soc. XXVI: 550, 1904.

TABLE 6.

No.	Mine	Precious Metal	Range of Ore	Available Manganese, as Indicated by Sphalerite
48	Waterloo	Silver	Less than 500'	(2) M
75	Goodenough	Gold	Less than 500'	(3) W
76	Ymir Yankee Girl	Gold	Less than 1200'	(3) W
77	Wesko	Gold	Less than 500'	(3) W
79	Reno	Gold	Less than 1200'	(2) W
80	Kootenay Belle	Gold	Less than 1000'	(2) Tr
81	Queen	Gold	Not yet known	(2) Tr
82	Bayonne	Gold	Not yet known	(1) W
90	Highland Bell	Silver	Not yet known	(3) M
92	Providence	Silver	Less than 700'	(3) W
105	Fairview	Gold	Plus 800'	(1)? Tr
132	Minto	Gold	Less than 700'	(1) M
	Pioneer	Gold	Plus 4000' (?)	(0) ?
	Bralorne	Gold		(0) ?
154	W.W.W.	Gold	Less than 500'	(3) W
155	Musketeer	Gold	Not yet known	(3) W
157	Mandalay	Gold	Less than 1000'	(1)? M
158	Privateer	Gold	Less than 1000'(?)	(3) M
159	White Star Zeballos	Gold	Less than 1000'	(3) Tr
160	Peerless	Gold	Less than 1000'	(2) W
161	Rey Oro	Gold	Less than 1000'	(1)? W
175	Cariboo Gold Quartz	Gold	Plus 1800'	(1) Mn virtually absent
176	Island Mountain	Gold	Plus 2000'	(1) Mn virtually absent
177	Cariboo Hudson	Gold	Not yet known	(2) Mn virtually absent
206	Premier	Gold, silver	Less than 1400'	(2) W

(0) Sphalerite or any other manganese-bearing minerals virtually absent.
(1) A little disseminated throughout the mine (-1%).
(2) Small amounts throughout the mine.
(3) Conspicuous throughout the mine.

sphalerite was precipitated and with it, much of the available manganese. This might well cause a sudden precipitation of the gold over a relatively restricted zone which, if the deposits are accepted as Tertiary, would naturally be related to the present surface. Incidentally, the deposits which do not bear any relation to the present surface are all probably pre-Tertiary in age.

In short, the relationship between the depth at which many of the British Columbia gold and silver mines bottom and the present surface can be explained, not on a basis of supergene, but of hypogene enrichment brought about by the precipitation, with sphalerite, of the manganese necessary to carry the gold in solution. As a correlation of the above, many of the gold and silver deposits in British Columbia may eventually be found to have been deposited in the Tertiary Era, and this is quite compatible with the geological evidence which is at present available.

Whether or not this idea has merit, it should at least serve as a basis for further observation.

SUMMARY AND CONCLUSIONS.

1. Most of the specimens which we examined came from Canada, and the majority of the remainder came from outside North America; so it is only possible to compare some of our conclusions with those of Stoiber, who

obtained most of his samples from the United States. Fortunately, samples of sphalerite from several localities were examined both by Stoiber and by ourselves, and on these samples our cadmium, manganese, gallium, germanium, and bismuth determinations checked satisfactorily. There is evidence to suggest that, for technical reasons, our indium determinations are less sensitive than are those of Stoiber. Other elements were, in general, not studied on a comparable basis.

Our general conclusions as to the type of deposit in which the above elements are apt to be most concentrated, are in agreement with those of Stoiber.

2. British Columbia and the Yukon have decided minor element characteristics, being high in tin and gold, and low in gallium, germanium, and vanadium.

3. Metallogenetic provinces or zones are of primary importance in establishing the minor element content of sphalerite. Within a metallogenetic province or zone, the temperature and type of the deposit in which the sphalerite occurs are important, but not determining factors.

4. There appears to be a tendency for each mining camp in Western Canada to exhibit a characteristic assemblage of minor elements. This tendency is reflected in part by the minor elements which appear in sphalerite. There are several instances of one or more mines situated on the same, or intimately related lodes, exhibiting a striking similarity in their minor element content. However, in view of the fact that sufficient collaborative results are not yet available, no final conclusions relative to most of these minor areas may yet be made. Nevertheless, further work may profitably be carried on in this field: there is every indication that detailed studies will show that each important orebody has a characteristic mineral assemblage and, furthermore, a characteristic minor element distribution in those minerals.

5. Variations of the minor element content of sphalerite taken from different depths of one vein or lode have not been studied, and this aspect should also be investigated in the future.

6. Sphalerite is a satisfactory pathfinder for tin. Unfortunately, much of the tin in British Columbia ores occurs in the form of stannite, which is, of course, much more difficult to treat than cassiterite and which, in fact, cannot be treated economically at the present time in the ores of any of the deposits so far discovered.

7. Incomplete evidence strongly suggests that a relatively high manganese bearing sphalerite may indicate that a gold or silver deposit will not persist to depths of more than one thousand to fifteen hundred feet.

Limited, and the Cariboo Gold Quartz Mining Company, Limited, made scholarship funds available for these studies.

The Department of Mining and Metallurgy permitted us to use their facilities, the Department of Physics placed their Hilger Medium Quartz Spectroscope at our disposal, and the Board of Governors of the University provided some of the necessary funds for equipment and supplies.

The members of the Department of Geology and the Geological Discussion Club of Vancouver provided much timely advice and criticism. The authors assume full responsibility for the conclusions at which they have arrived, but gratefully record the above assistance and cooperation.

DEPARTMENT OF GEOLOGY,
  UNIVERSITY OF BRITISH COLUMBIA,
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THE ABYSSAL *VERSUS* THE MAGMATIC THEORY OF ORE GENESIS.

CHARLES HENRY WHITE.

ABSTRACT.

If the earth in the beginning cooled down from a fluid state, by the time a solid crust had formed, gravity, diffusion, and the order of chemical combination in a cooling system, would have differentiated and segregated silicates and the heavy metal ores in zones, or layers, so widely separated that the small volume of magma entering a magma chamber in the outer crust of the earth would not be likely to contain, except in traces, the great variety of disparate elements found in an ore-bearing terrane.

Since practically all deposits of primary ores of the heavy metals have entered the host rock through fractures, shears, fissures, or open pores, existent in the rock prior to the introduction of the ore-bearing fluid, and since the host rock is more often sedimentary or metamorphic than igneous, it is logical to conclude that the relation between ore deposits and igneous intrusives is structural rather than genetic.

Theories of Ore Genesis. The most useful guide in the search for ore is a correct theory for its origin and mode of occurrence. Every prospector, even the most inexperienced, would be at sea without a theory and is not reluctant to formulate one on the basis of whatever experience he may have had. Soon after the discovery of the Rand Banket (Africa), about 60 years ago, an engineer whose experience had been limited to gold-bearing quartz veins, after an inspection, pronounced it a very unpromising prospect,[1] yet the district has yielded more than 10,000 tons of gold and the annual production is worth 500 million dollars.[2]

Theories of origin of certain types of supergene deposits due to the action of descending solutions have been so well established that they may be stated as principles, or laws, of nature; but, of the several theories proposed for the origin of hypogene ores of the heavy metals, none has received universal acceptance.

The earliest definitely formulated theory of ore genesis is probably that proposed by Agricola nearly four hundred years ago. He held that water, chiefly of surface origin, circulating in the rocks dissolved out ores and carried them in solution to open fissures where the solutes were precipitated to form veins.[3] Some three centuries later this theory was revived, and, with slight modification, became the briefly popular lateral secretion theory. The Neptunists, whose chief protagonist was Werner (1775), held the short-lived hypothesis that mineral veins were formed by descending percolating waters, derived from the primeval universal ocean. These two hypotheses lacking either rational theoretical basis or convincing supporting evidence have been rejected.

Descartes (1664) suggested that the ores came up as exhalations from a hot metalliferous shell below the crust of solid rock. This theory, which might be called the Cartesian, but is generally referred to as the "deeper than

crust" origin or abyssal theory, has had few adherents, but, in my opinion, has a more rational basis than the more recent and vastly more popular magmatic theory.

The magmatic theory for the origin of ores is based upon the assumption that when magma enters a magma chamber it is more or less a uniform mixture of all the elements found in the ores and in the slightly older igneous intrusives that occur in the district; and that these rocks and ores were differentiated from the mixture as it cooled. This theory, which had its inception somewhat more than a century ago, has been so generally and confidently accepted, that when no igneous intrusive can be found which might reasonably be suspected of being the mother of the ore, one is unscrupulously postulated to be in hiding just out of sight.

While there have been differences of opinion and much discussion as to the method of differentiation in the magma chamber, the more fundamental and important question of how a body of magma so limited in size could be so all-inclusive after the long period of differentiation in the fluid mass of the earth as a whole before a solid crust began to form, has been generally ignored.

Differentiation of the Elements in a Cooling Planet. If there was a time at the beginning of the fluid state of the earth's development when its component materials were uniformly mixed throughout its mass—which seems most reasonable [4]—it is undeniable that by the time a solid crust began to form a marked differentiation and segregation of its components would have taken place; the lighter on the outside, the heavier below, with increasing density toward the center. Even while in the gaseous state the process would have been initiated and would have proceeded according to the laws of gravitation and diffusion. Gravity being proportional to the masses and diffusibility inversely proportional to the square root of the density of particles, would tend to draw the heavy particles toward the center and drive the lighter ones toward the outside.

Order of Chemical Combination. It is evident that differentiation would be effected by physical forces alone while the temperature was too high to permit chemical combinations to take place but when the loss of heat permitted chemical union of the elements, differentiation was definitely promoted, in fact impelled by the laws governing chemical combination in a cooling system.[5] According to these laws, only combinations can take place that give out heat, and those that give out the greatest amount of heat take place first. For example, when copper sulphide and iron are heated together in a closed vessel to a high temperature, the copper sulphide dissociates and when cooled down the sulphur does not return to the copper but combines with the iron instead; the heat of formation of the monosulphide of copper is only 48.6 kj. while that of the monosulphide of iron is 96.9 kj.[6]

It appears, then, that the order in which the elements united as the earth cooled down may be revealed by arranging the heats of formation of compounds in descending numerical order as in Table 1.

This table shows in a general way how heats of formation of compounds tend to decrease as the atomic weights of their component elements increase.

The numbers in the table, except the atomic weights and densities, are

TABLE 1.

	Density	Atomic weight	F 19.0	O 16.0	Cl 35.458	S 32.065	Br 79.916	Se 79.2	I 126.932	Te 127.5
Li	.53	6.939	609	593	407		350	399	272	
Ca	1.5	40.07	599	634	409	475	339	370	269	
Na	.97	22.997	570	415	411	376	361	291	290	
K	.86	39.095	561	361	436	369	393	357	329	
Mg	1.74	24.32	552	610	320	344	259		181	
Al	2.7	26.96	444	556	232	481	176		99	
Averages	1.38	26.73	557	528	369	409	313	354	240	
Mn	7.2	54.93	431	380	235	198	190	114?	160	
Zn	7.14	65.38	402	353	208	192	163	140	104	139
Fe	7.8	55.84	371	268	171	96	163	80	99	32
Cd	8.6	112.41	361	273	194	142	153	90?	101	66
Ni	8.9	58.69	358	242	156	87	111	56	87	45
Pb	11.34	207.20	333	219	179	93	138	99	87	23?
Averages	8.35	92.41	376	289	190	134	153	96	106	61
Sn	7.31	118.70	327	292	169	100	128		75	
Sb	6.68	121.77	302	221	127	50	85		61	
Cu	8.9	63.57	292	146	136	48	103	20	66	
Ag	10.5	107.88	203	29	126	21	99	−4	62	17
As	5.7	74.96		218	101	40	64		20	
Hg	14.19	200.61		91	111	45	103	17	46	
Pt	21.45	195.23			71		42		17	
Au	19.3	197.2		−18	43		19		4	
Averages	11.75	134.99	281	122	110	51	80		44	
H		1.007	268	242	92	22	36	−66	−25	−142

heats of formation in kilojoules where only one atom of the anion is required in the formula of the compound. With polyvalent elements requiring more than one atom of the anion in the formula of the compound, the number in each case is not the heat of formation but the fraction obtained by dividing the heat of formation by the number of atoms of the anion involved; that is, the order indicated by the numbers in the table represents the order in which the anions would combine with the metals to yield the greatest amount of heat per unit of anion. For example, although the heat of formation of magnesium chloride ($MgCl_2$) is 641 kj. and that of lithium chloride (LiCl) is 408 kj., two atoms of chlorine are involved in the molecule $MgCl_2$ while only one atom of this anion is united with the monovalent lithium atom; therefore, if the chlorine had a free choice it would unite with the lithium in preference to the magnesium, or to any other element that stands below it in the series.

Table 1 shows that the lighter elements, which would be in juxtaposition in the outer envelope of the earth, would be the first to unite to form compounds while the less chemically-active heavy metals with sulphur, selenium, and tellurium would fall by gravity below the highly exothermic compounds, to unite in depth when permitted to do so by the reduction of temperature.[7]

Density Increases with Depth. Differentiation of the earth's materials into zones, or shells, increasing in density with increasing depth is not only

inferred from the laws governing the chemical and physical forces acting upon the earth while in a fluid state, but the inference is verified by such information as exists concerning the nature of the earth's crust and its interior. The specific gravity of the earth as a whole is about 5.52. The density of the surface rocks is about 2.65 and of the deeper seated rocks from 2.9 to 3.4; therefore, the density of the nucleus must be very much more than 5.52. Helmert [8] estimates that the density of the matter of the center of the earth is about 11.2. Of all the elements and combinations of elements only lead, thallium, mercury, tungsten, uranium, gold, and the platinum metals have densities greater than 11.

H. S. Washington [9] suggested that "the central core, the real nucleus of the earth, is composed of the metallogenic elements, that is, the elements or metals of the highest atomic weight, either as native metals or possibly in the form of selenides, tellurides, arsenides, antimonides, bromides, and iodides." On the other hand, the data in Table 1 (densities and heats of formation) indicate that no anion would be likely to penetrate deeper than the iron-nickel zone.

From a study of earthquake waves, Weichert [10] found that the volumes of the nucleus and the envelope are roughly equal, that is, the radius of the nucleus is 3,107 miles and the thickness of the envelope, 855 miles. Assuming a density for the nucleus of 7.8 which is the density of pure iron, the density of the envelope would have to be 3.2 to give an average of 5.5 for the whole earth. But since the heaviest silicates would not average more than 3.2 and the surface rocks about 2.65, the whole envelope would average quite below 3.2; therefore, the nucleus must be denser than 7.8. There appears to be a gradual increase in density downward in the silicate envelope and there is probably a similar increase in the metallic nucleus from an outer iron zone to deeper zones of heavier metals.

Earth's Core Denser than Meteorites. The fact that some meteorites are composed almost entirely of iron and nickel has led cosmogonists to infer that the nucleus of the earth may have the same composition—an assumption hardly justified since the evidence suggests rather a disparate than an identical composition for the nuclei of cosmic units. The moon, for instance, with a density (3.3), not so great as the heaviest silicates, probably has not an iron nucleus. The density of Mars is 3.9; its nucleus is probably less dense than the iron meteorites. The densities of the planets beyond Mars (Jupiter, 1.4; Saturn, 0.7; Uranus, 1.3 +; Neptune, 1.3) [11] show that they are chiefly, if not wholly, gaseous.

Meteors passing through the earth's atmosphere often explode. The fragments that reach the earth are in many cases entirely of the stony variety, in others, entirely metallic, and in still others, partly stony and partly metallic. More than 90 per cent of meteorites are of the stony variety, composed chiefly of heavy iron-magnesium silicates like olivine and bronzite. Ninety-nine analyses of stony meteorites showed an average of 1.85 per cent sulphur, present as iron sulphide.[12] Meteors have been observed to leave a luminous trail; whether this is a vaporization of lighter silicates that may originally have surrounded the body, as has been suggested,[13] is not known,

but the composition of meteorites as they reach the earth, suggests that they may be fragments of a planetoid, or other heavenly body, with nuclei similar in composition to the earth's iron-nickel and adjacent silicate zones.

Errors Due to Disregard of Chemical Law. While due consideration has heretofore been given, in geological literature, to the effects of physical forces —gravity, diffusion, heat—active upon the cooling earth, the chemical law of combination effective in a cooling system has been generally ignored. This is true not only with reference to discussions of theories of ore genesis but in other fields as well, and this neglect has led to much unbridled imaginative writing that now appears indefensible.

F. W. Clarke,[14] discussing the origin of petroleum, wrote: "If the molten globe had at any time a temperature like that of the electric furnace, carbides, silicides, nitrides, etc., would be the earliest compounds to form, and oxidation could not begin until later." Table 2 shows comparatively the heats of formation of carbides and oxides. The silicides and nitrides, like carbides, are feebly exothermic. It is not likely that carbides, silicides, or nitrides could form in the presence of oxygen; the oxides are so much more highly exothermic. The carbides of iron and nickel are even endothermic (-19.25 kj. and -160 kj. respectively), and carbon and silicon would go to oxygen in preference to any metal (CO_2 395 kj., SiO_2 842.6 kj.).

TABLE 2[6].

HEATS OF FORMATION OF OXIDES AND CARBIDES

Oxides		Carbides	
SiO_2	842.6	SiC	6
MnO	380	Mn_3C	52
FeO	268	Fe_3C	-19.25
NiO	242	Ni_3C	-160
UO_3	1214	UC_2	121
Al_2O_3	1630	Al_4C_3	341
CaO	634	CaC_2	61
Li_2O	593	Li_2C_2	57
ZrO_2	748	ZrC	146

In an article on "The Physical Chemistry of a Cooling Planet" P. G. Nutting [15] regards as most likely the early formation of carbides of boron, calcium, chromium, molybdenum, silicon, uranium, and vanadium, and refers to probable large quantities of "deeply buried carbides" below the outer crust of the earth, and he states further: "At 2,500 degrees there could have been no hydrocarbons or carbonates; the question is the probable division of carbon between the dioxide and the metal carbides, particularly silicon carbide, which must have been abundant in vapor form since it sublimes far below its melting and dissociation temperatures." He also says, "In a contest between oxygen and silicon for the carbon it is difficult to say which would be favored but both compounds would be present." The great disparity between the heats of formation of oxides and carbides as shown in Table 2 would apparently preclude the formation of carbides in the presence of oxygen.

The belief has been held, particularly by J. Joly [16] and Alexander Winchell,[17] that much hydrochloric acid was held in the atmosphere when the silicate crust began to form on the earth, but this does not seem possible

since the heats of formation of the chlorides of the alkalies are more than four times as much as that of HCl (Table 1), and free hydrogen would have joined with oxygen instead of with chlorine since that combination would have yielded more than twice as much heat.

Separation of Ore Magma from Rock Magma. As stated in the beginning, the magmatic theory, as described by its adherents, specifies that ores are differentiated from discrete bodies of magma after they have been injected into magma chambers in the solid crust of the earth. The abyssal theory also implies differentiation from magma, but its adherents believe that differentiation took place in the earth as a whole while it was cooling from a fluid state, and that the ores of the heavy metals for the most part were depressed to abyssal depths before a solid crust was formed, and were later carried up and deposited in the crust when it was fractured by crustal movements down to the ore reservoir.[18]

The emanations from volcanoes, fumeroles, and hot springs have been cited as evidence of a "relationship between mineral deposits and magmas," [19] but the preponderance of evidence favors a relationship with magmas at abyssal depth rather than with those confined to a magma chamber.

What seems the most rational explanation of the source of the volatile emanations from volcanoes—water, chlorides, etc.—and the high content of sodium in lavas, is ocean water that, through fractures in the sea floor, joined the magma as it rose from abyssal depth. While many ore minerals have been detected in volcanic emanations, their paucity indicates that the magma, at least in part, came from a silicate zone above the ore zone proper, or from the transition zone between rock magma and ore magma.

The sulphur deposited by fumeroles probably started from a great depth in the sulphide zone, chiefly as iron sulphide, where, apparently, there could have been no water. When it came into the silicate zone where water, as water of constitution, was encountered, the iron took oxygen from the water and gave its sulphur to the hydrogen in exchange. As the hydrogen sulphide approached the surface and met atmospheric oxygen, the oxygen seized the hydrogen, threw down the sulphur and escaped as steam.

Contact Metamorphic Ores Probably Not Indigenous. It has generally been assumed by magmatists that the ores in what are known as contact metamorphic deposits have been precipitated from extracts from the magma that produced the metamorphism. There is weighty evidence against this view. The strictly contact metamorphic minerals (non-metallics) are composed of elements that pre-existed in the adjoining unmetamorphosed rock, which recombined through the agency of the heat from the intrusive into forms to which the new environment was more congenial. This appears to be the normal condition where profound fissuring has not followed metamorphism. By far the larger number of occurrences of contact metamorphism are devoid of ore deposits; where sulphides appear to be syngenetic, they occur in little more than traces, but where they form ore deposits, the ore appears to have come in through post metamorphic fractures or fissures, accompanied by the usual hydrothermal rock alteration, such as sericitization, chloritization, etc. Shrinkage of the igneous intrusive on cooling opens fractures, affording pas-

sage for ore-bearing fluids if, and when, later crustal movements open fissures down to the sulphide zone, which, as we have seen, is more likely to be at abyssal depth than in a magma chamber beneath a frozen silicate intrusive.

Origin of Ore Magma Deeper than that of Rock Magma. From the foregoing, the conclusion seems inevitable that the succession downward when the silicate crust began to form was, first, light silicates followed by heavy silicates, oxides of the heavy metals, sulphides, selenides, tellurides, and other feebly exothermic compounds of the heavy metals, and finally the heavy metals. The crust cooled and thickened by freezing of the subjacent magma. Shrinkage due to consolidation of the magma necessitated folding or wrinkling and breaking of the crust to permit it to rest upon the shrinking core. An open fracture in the crust would permit an outflow of the subjacent magma; therefore, in general terms, the thicker the crust, the more basic the liberated magma. It is a significant fact that in a large majority of the copper districts of the world the latest magma injected into the terrane prior to the advent of the copper-bearing fluid is decidedly basic, usually in the form of dikes or sills, often carrying minute disseminations of syngenetic sulphides.

Hypogene ore-bearing fluids can come into the terrane only through fractures or porous beds in the crust. Hypogene deposits in detrital rocks probably came into the sedimentary beds in depth through cracks in the underlying igneous crust. That seems the most reasonable explanation for deposits like Lake Superior Copper, Corocoro, Boleo, Rhodesian-Congo Border, Mansfeld Copper (through the underlying sandstone), and the Rand Banket (gold in pyrite).

Ore-bearing fluid that rises through fractures in the crust is often, though not always, preceded by rock magma. There may be only one such intrusion or extrusion, or there may be a succession at long intervals, with usually increasing basicity, followed, as stated above, by the rise of the ore-bearing fluid. In several copper-bearing districts no intrusive has been discovered, such as the Vermont district, Copperopolis, Boleo, Corocoro, Casapalca, Ashio, Besshi, Kosaka, Bor (Yugoslavia).

Because several districts in the Andes and in Arizona contain important intrusions of monzonite, it has been suggested that magma of that quality has a genetic relation to the ore. Many of these districts, I believe all those in Arizona, have later intrusions of much more basic magma, injected much nearer the time of deposition of the ore, and probably came from much nearer the place of origin in the depths of the earth than the monzonite. Following are copper districts in which pre-ore basic intrusives have been reported: Kennecott, Bisbee, Christmas, Globe, Miami-Inspiration, Ray, Jerome, Morenci, Magma, Chino, Engels, Walker, Shasta, New Jersey districts, Virgilina, Ducktown, Copper Mine River, Sudbury, Eustis, Noranda, Normetal, Britannia, Flin Flon, Nacozari, Rhodesian-Congo Border, Messina, Yangtze Valley, Hitachi, Kyshtim, Cloncurry, Mt. Morgan, Outokumpu, Falun, Boliden, Mansfeld, Cyprus, and Rio Tinto.

Zonal Arrangement Suggests Abyssal Origin. The zonal arrangement of hypogene deposits around centers of mineralization also suggests an abyssal origin. Where tin and copper occur about a center of mineralization, as at

Cornwall (England), the tin (cassiterite) is nearer the center than copper, although tin stands above copper in Table 1. It will be noticed, however, that as regards the oxide, tin should be placed even above iron. Cassiterite, therefore, would form before magnetite and also before the sulphide of any heavy metal, and, owing to its high density (6.4–7.1) would sink into a zone below all metals that could rob it of its oxygen. Later, coming up to form an ore deposit, it would naturally lag behind overlying sulphides. Cassiterite is usually stained brown or black with oxides of manganese and iron; their heats of formation suggest that they are all formed about the same time. Cassiterite being non-volatile would move only with the host magma.

The heat of formation and the density of galena (7.2–7.7) would indicate that it would form before copper sulphide and fall, as does cassiterite, to a zone of safety, but owing to the volatility of galena,[20] it would sublime and seek safety in the opposite direction. It is this property of lead and zinc sulphides that places them in a zone of mineralization farther from the center than copper ores, where the rock is well fractured; and it is the same property possessed to a higher degree that drives stibnite and cinnabar still farther away.

Magmatic Theory May Mislead in the Search for Ore. The magmatic theory not only lacks natural law for its support but it is often misleading as a guide in exploration. Many intrusions have not been followed by mineralization, and many hypogene ore deposits apparently have not even a remote connection with intrusives. Hypogene ores come into the crust through open fractures or fissures, and by like channels rock magmas rise to or toward the surface. A body of magma cooling and solidifying in a magma chamber suffers material shrinkage. The intrusive will tend to withdraw especially from the upper contacts, producing open spaces or zones of weakness which later crustal movements would intensify and provide easy ingress of ore-bearing fluids.

The term ore-bearing fluid is used designedly to include both liquids and gases, for it would seem as if transportation above the vein-dike, or "plutonic," region would necessarily be at temperatures above the boiling point of water, and much of it above its critical temperature, therefore, the medium would be gaseous and the process would be pneumatolytic rather than hydrothermal. Sphalerite which is deposited far from centers of mineralization is believed to be carried in gaseous form. Newhouse has proved that sphalerite in the Tri-State District was deposited at temperatures of 115 to 135 degrees.[21] Even sulphur is deposited at the vents of fumeroles at temperatures above the boiling point of water. The assumption that water is the chief transportation agent of ores is open to question. The belief that magmas give off large quantities of water appears to be based upon the fact that vast quantities of water are ejected from volcanoes. As already mentioned, the evidence indicates that the chief source of volcanic water is the ocean. As I have pointed out elsewhere [22] ore magma when it starts on its journey from below the crust is probably devoid of water; that which accompanies it to the place of deposition is probably water of constitution, gathered from the rocks through which the ore passes in its upward course.

There seems little justification for adherence to the magmatic theroy. It is opposed by fundamental scientific law, and, in the search for ore, it may hinder rather than help. Experience has taught us that a district should not be abandoned because intrusives are absent, nor that a district is ore-bearing if intrusives are present. On the other hand, areas should be examined where there are probable breaks that may reach through the silicate crust to the ore zone.

The presence of intrusives proves that the crust has been fractured to the zone of molten silicates, and these fractures may or may not be directives to possible later fractures that may reach the ore zone. Not only is evidence strongly in favor of a structural rather than a genetic relation between intrusives and ore deposits, but searchers for ores of hypogene origin find it distinctly to their advantage to adhere to that belief and to be guided by structures wherever they may lead rather than by the nature of the country rock. Where the structure is not evident at the surface a significant break in the crust may be indicated by rock alteration due to hypogene emanations that have risen through a concealed fracture.

In the development of a science, pure or applied, less rational theories must yield to the more rational. To the great advantage of Astronomy the center of the Solar System was moved by Copernicus from the earth to the sun. In theories of ore genesis advantage has been gained as the hypothetical source of the ore has been moved successively from the waters of the ocean to the outer solid crust of the earth and then to intrusive bodies that came from the depths; now it seems most rational to carry it to the depths below the crust. If an intrusive is the mother of an ore body resting on its shoulder, then a bird's nest on the branch of a tree must be fruit of the tree!

SAN FRANCISCO, CAL.,
   Feb., 15, 1945.

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EFFECT OF HEAT ON METALLIC MINERALS.

P. E. AUGER AND OVIDE MAURICE.

ABSTRACT.

When minerals in polished sections are subjected to heat treatment, they are affected at temperatures which may be considered as characteristic of each mineral.

An electric furnace was built small enough to be placed on the stage of a microscope. Through the pyrex window at the top, the polished surface of the mineral may be observed continuously while the temperature rises inside the furnace. The temperature at which a colored film forms on the polished surface may be used to identify the mineral. This heat treatment also brings out a striking contrast between minerals which are otherwise difficult to distinguish under the microscope. This method is very helpful for mode analysis of ore minerals in polished sections. It is rapid, does not require a perfect polish and permits the determination of very small grains of minerals.

INTRODUCTION.

DETERMINATION of minerals in ore products has always been an important problem for geologists and mineralogists. There are several known methods which are widely used, but all present certain disadvantages which are difficult to overcome. One of these methods consists of etching the polished surface of the mineral with chemical reagents while the specimen is under the microscope. The main objection to this method is that the metallic parts of the objective are liable to be attacked by the liquid reagents or their fumes. Another difficulty is that in order to be sure of the results obtained by this method, the surface has to be free of scratches, which means a long careful polishing. Also the grains have to be large enough so that the drop of the reagent does not overlap unto neighbouring minerals. If the reagent (an electrolytic solution) rests on two minerals of different composition, it may set up electrochemical reactions which confuse the results obtained.

A. M. Gaudin [1, 2, 3] tried a new method which consists of dipping the whole polished specimen in various chemical reagents in order to stain the constituent minerals with a film of specific color which may be used for identification. This method is rapid and avoids the danger of damaging the objective of the microscope. However it is still difficult to use because it needs solutions which may initiate disturbing electrochemical reactions and because various delicate factors as: pH of solutions, temperature of the bath, the method for drying etc., may affect the results. In addition it requires an experienced operator who has had extensive practice with the method.

With this in mind, a method of identification was sought which would be dry, involving no handling of solutions; which could be used with success

[1] Gaudin, A. M.: Sulphide silver minerals. ECON. GEOL. 33: 143–147, 1938.
[2] Gaudin, A. M.: Staining minerals for easier identification in quantitative mineragraphic problems. ECON. GEOL. 30: 552–562, 1935.
[3] Gaudin, A. M.: Journal of Physical-Chemistry 41: 811, 1937.

even on exceedingly small grains of minerals enclosed in any other mineral, and which required no special skill or experience on the part of the operator.

It was considered that minerals could possibly be etched selectively by heat alone without the help of any chemical. This was tried and found to be successful for at least a large number of minerals.

APPARATUS.

For this investigation, a special type of electrical furnace was designed and built in the department of Geology of Laval University. The main purpose of this furnace was to heat the specimen to be studied while one of its surfaces, polished beforehand, was under microscopic observation. For this reason, the size of the furnace was limited to that of the diameter of the stage of the microscope and everything in it had to be made as compact as possible.

◨ Compressed asbestos

▨ Asbestos fiber

▦ Alundum

▦ Half-cylinder of steatite

Scale of Inches
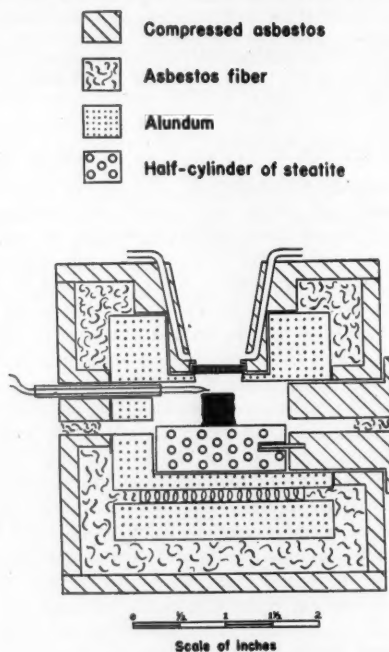
FIG. 1. Section of furnace.

Figure 1 shows a section through the furnace and Figure 2 a photograph of the apparatus in use with all the accessories.

The furnace is a cube, the base of which is 3.5×3.5 inches. It consists of an alundum core with a cylindrical internal chamber 2.5 inches long and 1 inch in diameter opened at the front. The front end is closed with a close

fitting cylindrical plug made of compressed asbestos. The rear end is provided with two small openings $\frac{3}{16}$ inch in diameter: one at the top through which the thermocouple is introduced into the internal chamber and one in the center for the introduction of gases other than air during the heating. There is a similar small opening in the center of the front door used as the outlet for these gases. The alundum core is enclosed in a cubic box made of pressed asbestos sheets. Asbestos fiber was used to insulate the outside container from the central core. The specimen to be studied rests on a half-cylinder of steatite which occupies the lower half of the internal chamber.
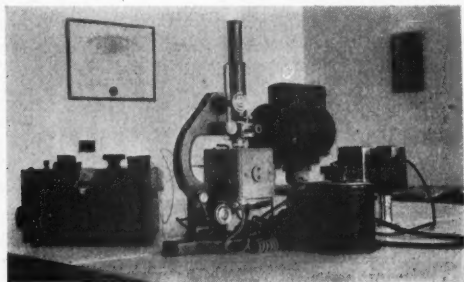
FIG. 2. Microscope assembly, with all accessories.

This can be rotated around its geometrical axis by means of two short steel rods which are fixed at the lower part of the door and fit into the end of the steatite half-cylinder when the door is closed. In this way, it is possible by rotating the door to bring the polished surface normal to the axis of the microscope during the heating process without opening the furnace. The half-cylinder of steatite is perforated in all directions so that the heat may be distributed uniformily throughout the inside of the furnace.

On top of the furnace there is an opening which has the form of an inverted cone one inch in diameter at the top and half an inch at the bottom. This hole is closed at the base by a pyrex glass which permits observation of the specimen in the furnace by lowering the objective of a reflecting microscope into the opening. To protect the objective when the temperature inside the furnace is high, a cooling device was added. This consists of two metallic tubes passing through the isolating material from the surface of the top cover of the furnace on both sides of the inverted cone down to the upper side of the pyrex window. Cold air is blown through these pipes to the glass surface and it comes up along the sides of the objective which is thus protected from over-heating. Since it happens frequently that the pyrex glass is stained by volatile matter escaping from the minerals at high temperature, it is important that it could be taken out and washed frequently. This is done by lifting the whole top cover of the furnace which is set with screws.

The electrical part of the furnace consists of resistances mounted in series. There are seven spiral resistances distributed evenly at a distance of $\frac{1}{4}$ inch

from the inner chamber with their axis parallel to that of the chamber. The resistances are made of chromel wire (B. and S. gauge: 26, diameter 0.0159 inch) with a total resistance of 54 ohms. This electrical unit is connected to the secondary coil of a transformer which is plugged into the standard 110 volt alternating current and the temperature is controlled with an Iron-Constantan thermocouple. The welded end of this thermocouple is introduced into the inner chamber through the upper hole at the rear end of the furnace and it is placed so that it is always a few millimeters above the polished surface of the specimen. The temperature is read directly on a calibrated potentiometer which gives a precision of $\pm 2°$ centigrade.

The temperature can be varied by means of a Variae-Type Transformer from room-temperature to 1000° centigrade. For most minerals investigated it is not necessary to reach above 650° centigrade since they are affected below this point.

POLISHING AND MOUNTING OF SPECIMENS.

The method used for polishing the specimens is that of the United States Geological Survey described by M. N. Short.[4] In the present case, two new polishing stages were added to the U.S.G.S. method: one on chamois with alumina powder and one on chamois without abrasive. These two stages were added to eliminate any grease and abrasive powder that may remain on the polished surface. They were also used after heating, to remove the film formed on the surface during the process of heating. When the film could be removed by rubbing on the chamois without abrasive, it was considered as non-adherent and this proved to be distinctive for some minerals.

In the course of the present studies, it is not necessary to have a perfect polish on the surface because a few striae do not hinder the formation of the colored film and do not change the final results. However a good surface facilitates the observations of the changes occuring on the surface during the heat treatment.

In several cases it was necessary to mount the specimens especially when these were of very small size. Numerous substances were tried, like bakelite, leucite and various refractory cements. The first could not stand the heat, the others fractured and crumbled or took too long to set. Finally it was found that plaster of Paris which sets rapidly and stands up well at high temperatures was the best material that could be selected in spite of the fact that it cannot resist the action of water. In most cases, mounting is not necessary; it is sufficient to cut the bottom surface of the specimen approximately parallel to the polished surface. Inside the furnace, this bottom plane rests on the half-cylinder of steatite which can be rotated until the polished surface is brought into a plane normal to the axis of the microscope.

EXPERIMENTS AND GENERAL OBSERVATIONS.

The experiment, repeated hundreds of times during this study, is very simple. A specimen of the metallic mineral is polished and placed inside the furnace. The temperature is then raised slowly and continuously following

4 Short, M. N.: United States Geological Survey, Bulletin 914: 27, 1940.

a definite time-temperature curve (Fig. 3). At a certain temperature, which seems to be definite for a certain mineral, colors begin to appear on the polished surface of the specimen. As the temperature rises above this point, the colors change continuously rising in order from yellow of the first order to red of the fourth order.
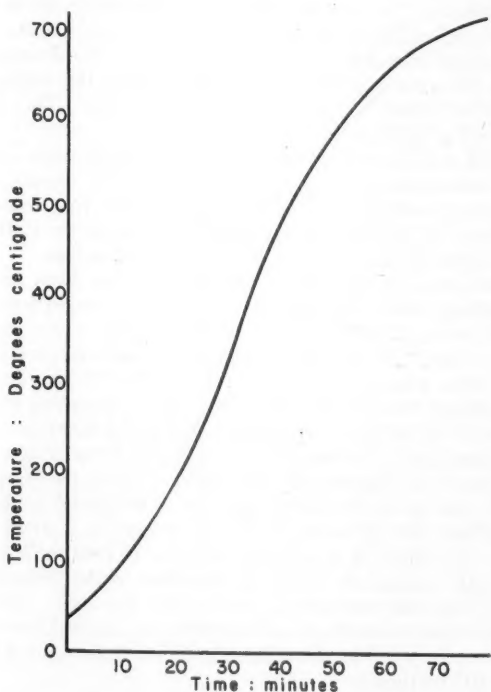
FIG. 3. Time-temperature curve.

This phenomenon is due to the formation of a thin film at the surface of the mineral, the colors changing continuously with the thickening of the film; finally the film cracks or the surface becomes opaque.

Oxidation of the mineral probably has an important role in thickening the film but it is not believed to be the only factor; heating was done in neutral atmospheres and the same results were obtained. J. S. Dunn [5] explains the thickening of thin films by a diffusion toward the surface of the elements of the mineral itself.

During the heating of the specimens, all changes which took place were observed and recorded but our attention was given mostly to those phenomena which seem to characterize the mineral under study. When the same phe-

[5] Dunn, J. S.: The oxidation of some copper alloys. Jour. Inst. of Metals 46: 22–48, 1931.

nomenon was repeated at every heating for the same mineral, it was noted as a means of identifying this particular mineral.

Six factors are of importance for the determination of minerals by heat treatment.

(1) *The temperature at which a thin film begins to be visible at the surface of the mineral.* It must be noted that a film is formed at the surface at a temperature below this point but it is too thin to be visible. This film protects the surface from further oxidation until the temperature reaches a point (point of affectation) when it no longer protects the surface. At this point, it begins to thicken and becomes suddenly visible. This is usually a fixed point for any given mineral.

(2) *The kind of coloration obtained.* There are three kinds of coloration: (a) a uniform coloration over the whole surface of the mineral, (b) a differential coloration in which the surface seems to fracture in a mozaic of grains of different colors, (c) an iridescent coloration in which the different colors appear as rings growing in order of color from central points.

(3) *The adhesive property of the thin film.* Some films are easily removed after heating; others are removed only after prolonged polishing.

(4) *The presence of volatile matter in the mineral.* This experiment is very sensitive to detect the volatile substances in a mineral; some specimens heated several times gave at the first heating results different from those of all the other heatings, which were very consistent. According to Schwartz [6] this may be due to the fact that certain minerals have an inversion point which is below the temperature of affectation. It was also found that volatile matters are often present in the minerals and that they affect the polished surface during the first heating by increasing the rate of formation of the thin film. This factor confirms the presence of volatile matter in a great number of minerals. For this reason, it was found advisable to heat the minerals for a certain time at 200° centigrade before placing them in the furnace.

(5) *The melting and sublimation point of the minerals.* Some minerals melt or volatilise between the limits of temperatures obtained here.

(6) *The inertness of some minerals.* Some minerals are not affected by heating up to 650° centigrade.

The time of heating is not an important factor. A rapid heating gives about the same results as a slow heating. Nevertheless, a slow heating is better if the point of affectation and the succession of interference colors are to be observed clearly. Heating according to the time-temperature curve shown in Figure 3 has given the best results in the present experiments.

The table below shows the minerals heated in order of their temperature of affectation. Temperatures between brackets indicate that the mineral has not a fixed point of affectation but rather a range of 25° to 30°. The temperature given in such cases is the mean temperature at which the mineral began to be affected for the specimens treated in the course of the present studies. The kind of coloring most likely to be seen and the adhesive character of the film are also noted in this table.

Note: Sign + indicates that the film is adherent to the surface; sign − in-

6 Schwartz, G. M.: Personal communication, 1944.

dicates that the film is non-adherent; sign − + indicates that the film is slightly adherent; absence of sign indicates that reaction is not conclusive.

TABLE.

Mineral	Point of Affectation (degrees centigrade)	Coloration
Bornite	18°	Uniform −
Pentlandite	110°	Uniform − +
Stromeyerite	(120°)	Uniform or Iridescent −
Native Copper	120°	Uniform +
Proustite	150°	Uniform or Iridescent −
Argentite	230°	Iridescent −
Antimony	(230°)	Uniform −
Chalcocite	(260°)	Uniform − +
Cuprite	260°	Uniform − +
Bismuth	270°	Fusion
Pyrrhotite	(270°)	Uniform +
Realgar	275°	Uniform
Covellite	275°	Uniform
Jamesonite	(290°)	Iridescent −
Pyrargyrite	(290°)	Uniform −
Stibnite	305°	Differential or Iridescent −
Chalcopyrite	(305°)	Uniform − +
Stannite	305°	Uniform +
Cinnabar	320°	Uniform
Enargite	(320°)	Uniform −
Galena	320°	Differential −
Malachite	(345°)	Uniform −
Loellingite	(345°)	Uniform or Iridescent +
Molybdenite	350°	Uniform −
Rammelsbergite	355°	Uniform +
Hausmannite	355°	Uniform or Iridescent − +
Sphalerite	(370°)	Iridescent −
Pyrite	(370°)	Uniform −
Arsenopyrite	(400°)	Iridescent − +
Benjaminite	(400°)	Differential
Breithauptite	420°	Uniform −
Tetrahedrite	(420°)	Uniform +
Ilmenite	(430°)	Uniform − +
Zincite	(430°)	Uniform − +
Chromite	(430°)	Differential +
Pyrolusite	430°	Uniform − +
Cobaltite	440°	Iridescent +
Gersdorffite	(480°)	Uniform +
Smaltite	(480°)	Uniform − +
Manganite	510°	Uniform − +
Niccolite	(515°)	Uniform +
Franklinite	540°	Iridescent −
Magnetite	(540°)	Uniform or Iridescent
Hematite ⎫ Limonite ⎬ Goethite ⎭	Not altered	

ADVANTAGES OF THE PRESENT METHOD.

This new method of etching minerals by heat has some advantages over all the other methods used and which may be listed as follows:

(1) It gives a microscopic view of the film while it is being formed In this way, heating may be stopped when the best contrast is obtained between the minerals.

(2) Very small grains of minerals are as easy to identify as larger grains.

(3) All the metallic minerals present in a specimen can be identified during the course of a single heating.

(4) The film produced is neater and more uniform than the film obtained by other methods.

(5) Little experience is required on the part of the operator.

(6) The temperature control is very easy.

(7) The process is dry with no solutions involved.

CONCLUSION.

The present study is far from complete since not all of the known metallic minerals were available. Yet, it gives an idea of the possibilities of the method for the determination of minerals. There are numerous minerals which in ordinary reflected light are difficult to distinguish from one another. These minerals are very easily distinguished after heating above the point of affectation of at least one of them. For example, the following may be mentioned :

(a) Pentlandite, easily distinguished from pyrrhotite because it is affected at a much lower temperature.

(b) Argentite, distinguished from stromeyerite by a slower thickening of the film.

(c) Proustite, altered at a much lower temperature than pyargyrite.

(d) Pyrite, on which the film formed is much more adherent than on chalcopyrite.

(e) Chromite, distinguished from magnetite, ilmenite and hematite by its differential coloration.

Since minerals are colored differently on the same polished section, this method has possibilities in the field of mode analysis of ore minerals. This method should also be helpful in studying the texture and relative ages of minerals.

The minerals heated in the furnace react in the same way as in the open tube. Volatile matter is more easily detected in the furnace because the gases have a coloring effect on the polished surface. In some cases they increase the rate of reaction at the first heating but in mode analysis this is advantageous, since it gives a better contrast between the minerals of the section.

In many cases in which the temperature of fusion of the mineral is low, this method gives the means of telling not only whether a mineral is fusible or not but also the exact temperature of fusion.

This method seems to open a wide field of investigation on polished surfaces of metallic minerals and further research may throw some light on the yet obscure problems of the behavior of some metallic minerals under heat treatment.

LAVAL UNIVERSITY,
    QUEBEC, CANADA,
        Feb. 15, 1945.

THE PREPARATION OF POLISHED THIN SECTIONS.

GEORGE C. KENNEDY.[1]

ABSTRACT.

The relations in ores between opaque and translucent minerals can not be determined satisfactorily by independent examination of either polished surfaces or thin sections. Previous attempts to prepare polished thin sections by Tolman and Rogers, and thinned polished sections by Donnay, appear not to have been entirely successful. Canada balsam, the cementing medium used, is not sufficiently tenacious to overcome the stresses imparted to the surface of the polished grain by the polishing process, which cause the grains to crackle and curl away from the glass slide. This paper describes two mounting media which largely overcome these stresses. These media are the thermoplastics glycol phthalate and Gelva V 7. Glycol phthalate is best suited to the polishing of thin sections on a cloth lap. Gelva V 7 is preferable if sections are to be polished on a Graton-Vanderwilt polishing machine. Photomicrographs of the results are appended.

INTRODUCTION.

THE author has recently been engaged in a study of the magmatic sulfide ores of Yakobi Island, southeastern Alaska. In the course of the study it became increasingly evident that the critical relations between the opaque minerals and the translucent rock minerals could not be determined satisfactorily by independent examination of either thin sections or polished surfaces. Opaque minerals can be identified with difficulty, if at all, in thin sections and methods of identification of translucent minerals in polished surfaces [2] are of little aid. With the help of many others, methods have been devised for the preparation of polished thin sections, which combine to a high degree the merits of both polished surfaces and thin sections.

HISTORY.

Attempts to combine the advantages of reflected light and transmitted light in the study of polished thin sections of ores were first reported by Tolman and Rogers,[3] and modification of the methods of Tolman and Rogers have been suggested by Donnay.[4]

The sections introduced by Tolman and Rogers were made like ordinary thin sections. A rock chip was cemented with Canada balsam to a glass slide and ground to the desired thickness. The section was then polished

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[1] Published with the permission of the Director, Geological Survey, U. S. Department of the Interior.

[2] van der Veen, R. W.: Mineralografie ook voor doorzichtige Mineralien. De Ingenieur, pp. 731–732, 1922.

[3] Tolman, C. F., and Rogers, A. F.: A study of the magmatic sulfide ores. Stanford University Press, pp. 75–76, 1916.

[4] Donnay, J. D. H.: Thinned polished sections. ECON. GEOL., vol. 25, pp. 270–274, 1930.

against a cloth lap. The polish takes the place of a cover glass and does not affect the appearance of the translucent minerals in transmitted light. These sections have numerous disadvantages. They are extremely difficult to prepare. The strains set up by the polishing are great and the harder minerals are almost always partly or entirely torn from the slide. In practice the sections are generally left thicker than ordinary thin sections and the desired polish is difficult to attain. However, good polished thin sections of the softer sulfide minerals, such as cinnabar and stibnite, have been prepared by the highly skilled preparators of the Geological Survey, Frank S. Reed and John L. Mergner, using the methods of Tolman and Rogers.

Donnay devised another type of combination section which he applied to the investigation of the ores from the Engels Mine, Plumas County, California. He describes his method:[5]

"The chip is polished first. It is then mounted on glass (with the polished surface against the mounting-glass) and ground down to the standard thickness of .03 mm. The thin slice is transferred onto a cover glass, so that the polished side now faces the cover glass. The covered section is finally remounted on another mounting-glass.

"The examination of the polished surface in reflected light, through the cover glass, is considerably hindered by internal reflections in the cover glass, which blur the contacts between the minerals and prevent satisfactory focusing. The difficulty is overcome by using oil immersion lenses. In this case, the three different media intervening between the polished section and the lens (i.e., Canada balsam, cover-glass, and cedar oil) have approximately the same refractive index and it is possible to obtain a perfectly sharp focus. The microscopic equipment should of course comprise low power oil immersion lenses (8 mm. lens, for instance). The limit of possible magnifications is controlled by the thickness of the cover glass, which should consequently be chosen as thin as possible."

The above method, as described by Donnay, is laborious, but it can be used if the sections are polished on an ordinary cloth polishing lap. Available evidence suggests to the present writer that polishing produces a superficial layer of stress in the polished surface, and crackling of the polished surface takes place immediately after the thinning of the section. Donnay states:[6]

"This results in a network of fine cracks which sometimes appear on the edges of the slide, in the softer metallic minerals (such as bornite and chalcopyrite), after completion of the thinning process."

Thus far the difficulty of mosaic crackling and of warping of the tiny mosaic plates appears not to have been overcome. Extended search for a mounting medium strong enough to hold the slice firmly cemented in place, carried on at Harvard, first by J. H. Moses and later by C. A. U. Craven, was unsuccessful. The characteristic difficulty developed regardless of whether the specimen was first thinned and then polished or first polished and then thinned. But the degree of warping was found to be inversely related to the "strength" of the cementing medium, Canada balsam being least satisfactory; and thus further search for a still better medium seemed justified. The crackling and warping were found to be present on both the opaque and the

[5] Donnay, J. D. H.: Op. cit., p. 272.
[6] Donnay, J. D. H.: Op. cit., p. 272.

transparent minerals, but are more readily detected on the surface of polished opaque minerals because, of their higher reflectivity. It was plain, however, that both the crackling and the warping took place after all work on the section had been completed; for the interference colors invariably showed the tiny warped plates to have the same thickness near their edges as in their central portions. Moreover, the crackling and warping was not always evident as soon as the specimen was finished, but some hours later could be detected. Strains caused by polishing appear to be cumulative and consequently deterioration of the quality of polish takes place with prolonged polishing beyond a certain optimum.

Discussions of methods of preparation of polished thin sections have been offered by Grondijs and Schouten [7] and by Rankama.[8]

<div style="text-align:center">PRESENT WORK.</div>

Most recent attempts to prepare polished thin sections have involved a search for a cementing medium superior to Canada balsam. This medium must bind the slice of rock to a glass slide firmly enough to prevent the deterioration of the section during the final stages of grinding or polishing.

Attempts have been made by C. A. U. Craven in the Laboratory of Mining Geology, Harvard University, and by the author in the Geological Survey laboratories to adapt lucites and other thermosetting plastics to this purpose, but none with sufficient adhesive properties was found. Several thermoplastics, suggested to the author by Dr. H. Insley, of the United States Bureau of Standards, were tried and among these, Gelva V 7 and glycol phthalate were found to be satisfactory. Either of these thermoplastics may be used in the place of balsam and a satisfactory polished thin section prepared after the manner of Tolman and Rogers. However, Gelva V 7 is a much tougher and more adhesive bonding medium than is glycol phthalate and must be used if the best no-relief polish is desired and the section is polished on a Graton-Vanderwilt lap.

<div style="text-align:center">GLYCOL PHTHALATE.</div>

Glycol phthalate may be obtained in small sticks from the General Electric Company, Schenectady, New York. However it can be prepared readily as described in the Handbook of Chemistry and Physics.[9] It is described as a transparent sealing resin, "prepared by heating together equimolal quantities of phthallic anhydride and ethylene glycol for 24 hours at 200° C. The resin softens at 95°–110° C. It is unaffected by water but slowly dissolved by organic solvent. . . ."

The glycol phthalate (20 × 75, batch 2444) obtained from the General Electric Company has the following properties. The index of refraction is 1.572 ± .002, and is very constant. The material can be fused and allowed to

[7] Grondijs, H. F., and Schouten, C.: Polished thin sections of ore and rock. Econ. Geol., vol. 26, pp. 343–345, 1931.

[8] Rankama, K.: An improved technique for the making of thinned polished sections. Econ. Geol., vol. 36, pp. 561–563, 1941.

[9] Handbook of Chemistry and Physics, p. 2388, 26 ed., Chemical Rubber Publishing Company, 1942.

cool several times without appreciable change in properties. The material is glassy and brittle at room temperature but is extremely viscous at 70° C. At this temperature a stirring rod can be slowly pushed into the plastic. At 100° C. the material is soft enough to be spread easily and to serve as a mounting medium. At approximately 160° C., bubbles in quantity are evolved from the molten plastic, which at that temperature has the consistency of syrup. The material can be successfully used as a mounting medium at any temperature between 100° C. and 160° C. On cooling it hardens immediately and has a glassy appearance. The plastic is readily soluble in acetone, which, on evaporation, leaves a non-adhesive soft paste.

Reed and Mergner of the Geological Survey have developed a method for the preparation of polished thin sections with this plastic. A rock slice about one-fourth of an inch thick and 1 inch square is sawed from the specimen. One face of this chip is ground for a few minutes on a lap charged with 600 carborundum. The rock slice is then placed face down beside a glass slide on a hot plate or a square of brass sheeting heated by a small bunsen flame. The slide and the face of the specimen are brought to a temperature of 100° C. to 150° C. A stick of the thermoplastic is run lightly over the hot slide. A thin layer of the plastic fuses and adheres to the slide. The specimen is then pressed into the hot plastic on the slide. It is important that the specimen and the plastic be at approximately the same temperature, for if the specimen is cold, chilling of the plastic and loss of adhesion to the specimen results. The time required to saw, grind and mount the chip is not more than ten minutes.

The chip is ground to the thickness of a thin section in three stages preliminary to polishing. The mounted chip is first ground on a 1 F carborundum lap until it is about .06 mm. thick, twice the thickness of an ordinary thin section. It is then ground on a lap charged with 600 carborundum until it is about .035 to .04 mm. thick. The final stage of grinding is by hand on a plate glass with 600 alundum abrasive. If the specimen is extremely friable the section is not ground quite as thin as would otherwise be the case on the 1 F carborundum lap. The total grinding time of these three stages is seldom more than 10 minutes and is generally 5 to 7 minutes.

The polishing operation is done in two stages. The section is polished first on a cast-iron lap, covered with medium grade duck cloth and charged with tin oxide. The final polishing is on a lap covered with Samson cloth and charged with magnesium oxide. These polishing operations take, on the average, less than 10 minutes, but if pyrite or other hard minerals are present somewhat longer times may be required. The section is held, during the grinding and polishing stages, in a lucite block, into one side of which a shallow recess the dimensions of the glass slide has been cut. A few drops of water on the back of the slide will hold it in place in the lucite block. This simple but highly successful holder is the invention of John L. Mergner, Geological Survey.

The quality of the polish that can be readily obtained on these sections is about the same as that obtainable on ordinary bakelite-mounted specimens. In some sections both translucent and opaque grains break into a coarse

mosaic pattern and curl up at the edges. However, this crinkling is not sufficient to interfere with the examination of the sections by reflected or transmitted light either at high or low powers, as the degree of curvature of the plates is not great. The crinkling is believed by the author to be a response to stress, after the pressure of the polishing lap against the section is removed, but while the mounting medium is still soft due to the heat generated by the friction of polishing. It is for this reason that balsam is not a satisfactory mounting medium, for it softens at a much lower temperature than glycol phthalate and lacks the strength and tenacity of the glycol phthalate. Cooked balsam has about the same viscosity at 45° C. as does glycol phthalate at 70° C.

The index of refraction of glycol phthalate (1.572) is regrettably high and the translucent minerals in contact with the plastic have an unaccustomed low relief. The high index of refraction is particularly disadvantageous if the section contains quartz and orthoclase; otherwise it assumes little importance. The author believes that for the preparation of most ordinary thin sections (the usual unpolished section with a cover glass) glycol phthalate may prove to be a mounting medium much superior to Canada balsam. Presumably it will not crack and turn yellow with age, as does balsam, for at ordinary temperatures volatiles are not evolved. There is less tendency for the chip to be torn from the slide during the grinding process, and hard minerals are less likely to be torn from the section. Skill and experience in preparing the medium, as is required in cooking balsam, is not necessary. These advantages are particularly important if inexperienced students are grinding the thin sections, though some difficulty may be encountered in cementing the cover glass to the completed section.

This medium has been used successfully in the preparation of ordinary thin sections in the laboratories of the Bureau of Mines, College Park, Maryland, U. S. Bureau of Standards and the Geophysical Laboratory, Carnegie Institute of Washington.

GELVA V 7.

The thermoplastic, Gelva, is a polyvinal acetate, manufactured by the Shawinigan Products Corporation, Empire State Building, New York City, and sold under the trade name "Gelva." It is a simple resin derived from vinyl acetate and produced by the polymerization of this pure monomer. The viscosity of a solution of Gelva and the softening point of Gelva depend on the size of the molecules in the polymer. Gelvas range from Gelva V 1.5, with a softening point of 65° C., to Gelva V 60, with a softening point of 196° C. Gelva V 7, with a softening point of 107° C., seems best adapted to use as a mounting medium for polished thin sections. Gelva V 7 is fluid enough to use as a mounting medium at 140° C., but it may be heated safely at 200° C., at which temperature it is slightly more viscous than syrup, before it begins to decompose and many bubbles are evolved. The viscosity of Gelva V7 at 110° C. compares to that of glycol phthalate at 70° C. and Canada balsam at 45° C. All three of these media soften over a considerable range of temperature, and no sharp melting point is determinable. Gelva may be fused
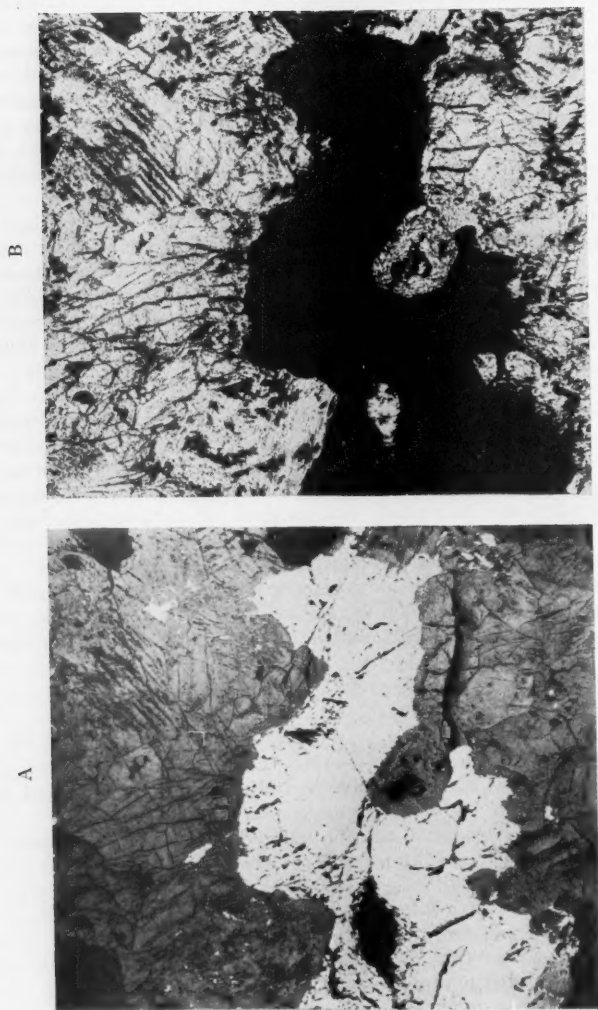
FIG. 1. A: Bleb of pyrrhotite, pentlandite and chalcopyrite (white area) surrounded by hypersthene. Normal vertical illumination, no transmitted light. ×9. B: Same area with no vertical illumination and normal transmitted light. ×9.

numerous times without noticeable change in its properties. Its index of refraction is very low (1.467) and is constant. It is soluble in most organic solvents but is insoluble in water, petroleum fractions and most oils.

Because of its higher softening temperature, higher viscosity and the difficulty of elimination of bubbles from the fused Gelva, rock slices cannot be cemented to glass slides as readily with Gelva as with glycol phthalate. Much the same method of mounting sections as previously described for glycol
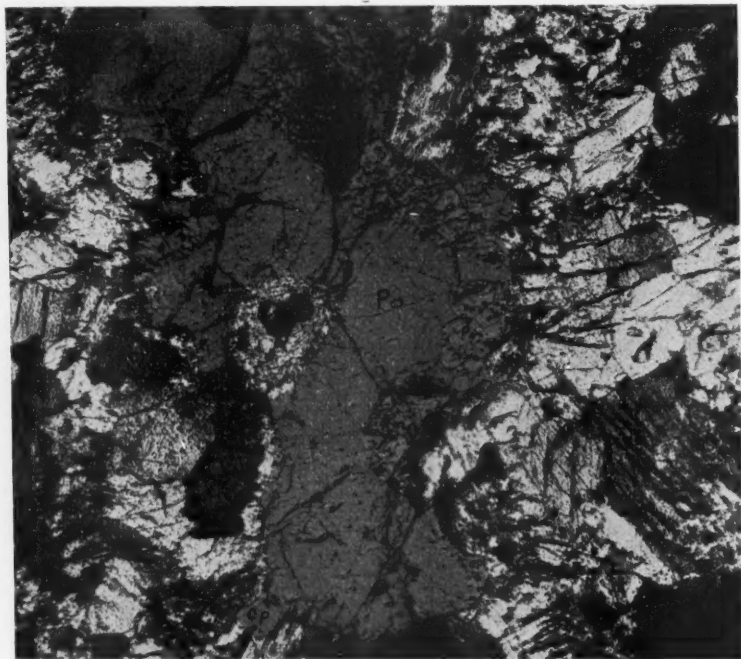
Fig. 2. Bleb of pyrrhotite (po), pentlandite (pn) and chalcopyrite (cp) surrounded by hypersthene. Same area as shown in Figure 1. Plane vertical illumination, crossed-nicol transmitted illumination. × 12.

phthalate, however, is applicable. Gelva is not obtainable in stick form, but as a crystalline powder crushed to about 8 mesh.

Sections mounted with Gelva may be placed in a lucite holder designed to receive them, or cemented to wooden blocks of the appropriate size, and polished on the Graton-Vanderwilt machine as are ordinary bakelite-mounted specimens. The superior toughness and tenacity of the Gelva over glycol phthalate is necessary to withstand the prolonged stresses set up during this type of polishing. Figures 1 and 2 show three differently illuminated photo-

micrographs of the same area of a polished thin section mounted with Gelva V 7. The polishing was done on a Graton-Vanderwilt machine, in the Harvard Laboratory of Mining Geology, and the photomicrographs were taken on the special microcamera designed to accommodate preparations of this kind, since it affords simultaneous transmitted and vertical illumination, with independent choice of normal, plane-polarized or cross-polarized light of each beam.

Polished thin sections are largely of value in studying textural relations of opaque minerals to translucent minerals and in studying the semi-opaque minerals, such as chromite. Their major disadvantage lies in the fact that, because of their thinness, they can be repolished but a few times for the removal of tarnish. For purposes of identification of opaque minerals they are not as satisfactory as the thicker bakelite-mounted specimens.

DISCUSSION AND COMMUNICATIONS

THE "SOLUBILITY" OF SILICA.

Publication of the results of an investigation on the hydrothermal solubility of silica by George C. Kennedy [1] in the Jan.–Feb. issue of ECONOMIC GEOLOGY for 1944 has provided further data relating to the system, SiO_2-H_2O, the phase-relationships of which must have an important bearing on theories of ore deposition and magmatic evolution.

In carrying out a similar investigation about ten years ago, [2] I allowed amorphous silica and water to attain equilibrium at a given temperature in a specially designed pressure vessel and then removed a known, filtered portion of the solution which was thereupon analyzed for silica. In his recent investigation, Dr. Kennedy deduced the solubility of silica from the loss of weight sustained by a bundle of silica-glass spicules when immersed in water in a bomb at constant temperature until equilibrium had been attained. The quantity of water placed in the bomb was so adjusted as to give a pressure of 300 atmospheres at each temperature.

Thus, while I employed the direct or positive method, Dr. Kennedy used the complimentary negative method and is to be congratulated on its development and on the provision of solubility data over a more extensive range of temperature. The lack of agreement between our respective results will be discussed later.

In his reference to my investigation, Dr. Kennedy reiterates the views of Frondel, [3] who criticized my results on the grounds that he had prepared undoubted sols having a silica concentration considerably below the solubilities reported by me for 25° and 100°. [4] He also found that turbid silica sols could be diluted to a silica content one-third of my reported solubility at 100° and could be boiled without decrease of turbidity. Moreover, he drew attention to the fact that Moore and Maynard [5] had described experiments at room temperatures with silica sols in concentrations as low as 30 parts of SiO_2 per million. By analogy with the results obtained by Svedburg and by Odén [6] for the Selmi and Raffo sols of elementary sulphur, Frondel suggested that I —and, earlier, Gruner [7]—had measured a peptization equilibrium which simulated a true solubility. Frondel concludes: "Coagulums of different particle size give different 'solubility' curves, the values increasing with decreas-

[1] Kennedy, G. C.: ECON. GEOL. 39: 25, 1944.

[2] Hitchen, C. S.: Trans. Inst. Min. Met. 44: 254, 1934–35.

[3] Frondel, C.: ECON. GEOL. 33: 13–14, 1938.

[4] Actually, I did not carry out solubility determinations below 100° but incorporated the results of Lenher and Merrill (J. Am. Chem. Soc. 39: 2630, 1917) for temperatures of 25° and 90° in my graph.

[5] Moore, E. S., and Maynard, J. E.: ECON. GEOL. 24: 391, 1929.

[6] Vide Weiser, H. B.: Inorg. Colloid Chem. I: 327–329.

[7] Gruner, J. W.: ECON. GEOL. 25: 700, 1930.

ing particle size. This correlates with the increasing solubility found by Gruner for quartz, chalcedony, and silica gel in the order named."

If this interpretation is, in fact, the correct one, it should apply equally well to Kennedy's results as to my own, since Kennedy *assumed* that the silica lost from the bundle of silica-glass spicules passed into "true" solution, *i.e.* a molecular dispersion of silica in liquid water. Owing to insuperable practical difficulties neither of us was able to investigate the state in which the silica existed in water at the various temperatures and pressures of the determinations.

According to general theory, one would expect silica, being the oxide of a non-metal, to unite with water to form one or more silicic acids, yet all attempts to demonstrate the stable existence of such acids in a free state have proved abortive. Apart from the fact that silica gel exhibits a continuous vapour pressure curve inconsistent with the existence of definite hydrates, Krejci and Ott [8] report that a freshly prepared sample of hydrous silica, which had at no time been heated above 100°, yielded an X-ray diffraction pattern of the cristobalite type. Pascal [9] analyzed three types of hydrous silica magnetically and found all three to behave like mixtures of the anhydrous oxide and water. A similar conclusion was reached by Le Chatelier.[10]

Of particular interest and importance in this connection are the observations of Mylius and Groschuff [11] which go far to show that, while silicic acids may be produced by the action of acids on alkali silicates, they are highly unstable compounds and rapidly polymerize with concomitant dehydration to produce silica sols and gels. The α-acid first produced by the action of HCl on $Na_2Si_2O_5$ at 0° passes through a dialyzing membrane and does not precipitate albumen from a white-of-egg solution. On standing some time or warming, however, it changes to the β-acid which precipitates albumen and possesses properties typical of ordinary colloidal silica. The transformation is accompanied by changes in the electrical conductivity and in the lowering of the freezing point. Thus, the α-acid was found to yield results corresponding to a molecular weight of 155, whereas that indicated for the β-acid approached 49,000. Observations tending to confirm the instability of silicic acids and their more or less rapid transformation into colloidal silica have been made by a number of investigators.[12]

If silica does not dissolve in water in the form of a stable silicic acid what are the probabilities of its forming a simple molecular dispersion in water, "true solubility," as assumed by Kennedy?, Moore and Maynard [13] state that silica is generally transported in natural waters as a colloid and not as acid ions and estimate that the average silica content of the rivers and lakes of the world does not exceed 15 parts per million. In the silica sols prepared by them containing 30 parts per million it is obvious that much of the silica must

8 Krejci, L., and Ott, E.: Jour. Phys. Chem. 35: 2061, 1931.

9 Pascal, P.: Compt. rend. 175: 814, 1922.

10 Le Chatelier, H.: Compt. rend. 147: 660, 1908.

11 Mylius, F. and Groschuff, E.: Ber. 39: 116, 1906.

12 Vide Mellor, J. W.: Comp. Treatise on Inorg. and Theoretical Chem. 6: 292; also Weiser, H. B.: Inorg. Colloid. Chem. 2: 225.

13 Loc. cit., p. 302.

have existed in colloidal form for the sols to be recognized as such. The indications are, therefore, that at normal temperatures the "true" solubility of silica in water is so extremely small as to be a negligible factor in supergene processes. It could not, for example, account for the large quantities of silica passing into solution in tropical countries.[14] Finally, in view of the tendency of silica particles to aggregate and coagulate, it seems probable that, as the number of individual silica molecules increased in the dispersion medium, they would aggregate to form composite particles of colloidal dimensions. This probability is suggested by the fact that when saturated silica "solutions" are cooled, the silica does not deposit but forms colloidal aggregates—a peculiarity which enabled Dr. Kennedy and me to determine its "solubility" with fair precision. Normally, saturation implies an equilibrium whereby as many molecules are deposited from the solution as enter it. In short, the condition of saturation is dependent upon the ability of excess molecules to leave the dispersion medium. In the case of silica this ability seems to be lacking.

It is thus possible to conceive of the "solubility" of silica in water, at a given temperature, as involving a two-fold equilibrium between the solid phase, singly dispersed molecules, and colloidal aggregates;

$$\text{solid phase} \; \underset{\longrightarrow}{\longleftarrow} \; \text{simple molecular dispersion} \; \underset{\longrightarrow}{\longleftarrow} \; \text{colloidal dispersion}$$
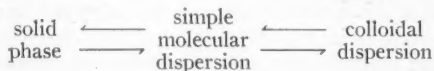
Such a conception closely approximates to the peptization equilibrium suggested by Frondel. Dr. Kennedy complains that my results combine, in unknown proportions, truly soluble silica (*i.e.* molecularly dispersed silica) and dispersed colloid. From the considerations outlined above, however, it would appear that this is the only type of solubility to be expected and that, taken by itself, true molecular solubility has no real significance in the case of silica. With characteristic perspicacity Le Chatelier wrote:[15] "On serait ainsi conduit à considérer la silice non plus comme un corps soluble dans l'eau mais au contraire comme un corps rigoureusement insoluble dont l'insolubilité même expliquerait l'extrême finesse."

Those who have investigated the solubility of silica have used either (*a*) amorphous silica or silica gel or (*b*) quartz, silica-glass, chalcedony, etc. The results of those who have used amorphous silica or silica gel fall, approximately, on the "solubility" curve given by me,[16] while results relating to the denser varieties of silica indicated under (*b*) fall, approximately, on the curve given by Kennedy.[17]

[14] In the Kakamega goldfield of Kenya, I was able to trace stages in the dissolution of quartz "floats" that had been exposed on the surface. The first stages were marked by a progressive increase in turbidity while a more advanced stage was characterized by the development of a saccharoidal texture due to the formation of hydrous silica along intergranular boundaries, flaws, cracks, etc. Thin films of hydrous silica were occasionally observed on the surface of exposed quartz blocks. This hydrous silica no doubt represents silica deposited from solution when the "float" dries out after rain. The only solvent that could have been involved was rain-water containing carbon dioxide.

[15] Le Chatelier, H.: loc. cit.
[16] Hitchen, C. S.: loc. cit., p. 273.
[17] Kennedy, G. C.: loc. cit., p. 31.

Many of the older determinations of the "solubility" of silica are unreliable owing to impurities derived from glass vessels and to other causes but it is noteworthy that, as long ago as 1852, J. Fuchs [18] found that, at ordinary temperatures, 0.013 parts of gelatinous silica dissolved in 100 parts of water, a result that compares favourably with the accurate determination of 0.016 parts at 25° by Lenher and Merrill in 1917.[19]   The results obtained by Gruner [20] for quartz, chalcedony, and silica gel in general show a "solubility" less than that indicated by the appropriate curves of Kennedy and myself, though his results for silica gel are always much greater than his corresponding results for quartz and chalcedony.   It would appear, however, that Gruner made no allowance for the condensation of water in the vapour phase which, during the cooling of the bomb at the conclusion of the experiment, would dilute the solution and thus yield a low result.   In a preliminary notice of investigations on the solubility, transport and crystallization by means of the vapour phase, Ingerson and Morey [21] state (with regard to the solubility of amorphous silica), "The point at 300° fits Hitchen's curve very well." They also note that "about half as much quartz as amorphous silica goes into the vapour phase."

The very much greater "solubility" of amorphous and gel silica as compared with that of the denser varieties of this substance has thus been established by various workers at various times and in various countries.   Moreover, with proper experimental care the results are repeatable and may be regarded as characteristic.   Although metastable forms such as cristobalite and silica glass might be expected to have a somewhat higher solubility than the stable form, low-quartz, over the normal and hydrothermal ranges of temperature, the actual discrepancy is so great that it would be difficult to explain if we were dealing with a case of simple or "true" solubility.   In the case of the hydrophilic colloids of sulphur, the behaviour of which is, apparently, closely analogous to that of silica "solutions," it has been shown by Odén [22] that particle size has a most important influence on the "peptization solubility" and it is this factor, probably more than any other, that is responsible for the difference of "solubility" of the several forms of silica—as suggested by Frondel in the passage quoted above.

In a series of experiments recently carried out by Wyart [23] it was found that when powdered silica glass was suspended in the vapour of distilled water in a bomb, some development of metastable cristobalite took place only in the neighbourhood of the critical temperature (374°).   When, however, the vapour was generated from a dilute potash solution, development of cristobalite occurred at 335° while at 340° and over quartz crystallized.   These observations are interpreted by Wyart as indicating that the appearance of quartz is dependent upon increasing the dissolving power of the water either

18 Fuchs, J.: Liebig's Ann. 82: 119, 1852.
19 Lenher, V., and Merrill, H. B.: loc. cit.
20 Gruner, W. J.: loc. cit.
21 Ingerson, E., and Morey, G. W.: Abs. Am. Geophys. Union, Pt. II, p. 504, Aug. 1941.
22 Odén, S.: "Der Kolloide Schwefel" (Nova Acta Reg. Soc. Scient. Upsaliensis, Ser. IV, Vol. III, No. 4).
23 Wyart, M. J.: Bull. Soc. Min. 66: 479, 1943.

by raising the temperature (though at 374° he only succeeded in obtaining cristobalite) or by the addition of a small quantity of potash. His experiments place on a more precise basis the general experience of the French geochemists of the 19th century who found that the appearance of quartz under hydrothermal conditions usually depended on the presence of impurities, especially alkalies, in the bomb charge.

It would appear, therefore, that all forms of silica in pure water exhibit a "peptization solubility" at least up to the critical temperature and that the crystallization of quartz in nature is dependent upon the presence of small quantities of alkali and, possibly, other and as yet undetermined impurities.

The broader implications of the subject can only be dealt with very briefly. Relying on my determinations of the hydrothermal "solubility" of silica, Bichan [24] has drawn attention to the inadequacy of hydrothermal solutions to deposit the vast amounts of quartz present in ore deposits nor have his arguments been invalidated by the recent determinations of Kennedy. In the light of the considerations set out above this inadequacy becomes even more apparent. On the other hand, it would be a mistake to regard the rôle of hydrothermal solutions as of little or no consequence in respect of ore deposition as a whole for they have undoubtedly been responsible for a number of interesting and important features, including wall-rock impregnation and alteration, metasomatic replacement, and the redistribution and recrystallization of material. Hydrothermal solutions do not appear adequate, however, to account for the origin of the more massive types of quartz vein or quartz-dike which, in many ore deposits, constitute a framework upon which other features have been superimposed by succeeding phases of mineralization.

It is to be hoped that further exploration of the silica-water system, especially the silica-rich end of it and the influence upon it of small amounts of alkali and other impurity, will furnish the answer to a problem that has confronted Geology since its inception.

C. STANSFIELD HITCHEN.

LONDON,
Mar. 15, 1945.

[24] Bichan, J. W.: ECON. GEOL. 36: 212, 1941.

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RALPH E. DIGMAN.

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NOTES AND NEWS

Dr. Heinrich Ries, professor emeritus of geology at Cornell University, received the honorary doctor of science degree at Alfred University's recent commencement exercises. The degree was conferred "In recognition of a lifetime and devoted service in writing, teaching and organization and research in the twin fields of ceramics and geology." Dr. Ries joined the Cornell faculty in 1898, was made a professor in 1906, and head of the Department of Geology in 1914, filling that position until 1937. He retired in 1939. His retirement, however, consists of a voluntary daily schedule of research in McGraw Hall. During his career he has written over 200 publications, including textbooks and reference books which are considered as standard texts in their fields.

D. L. Scholtz is President of the Geological Society of South Africa.

The Draper Memorial Medal has been awarded to F. Dixey, Director of the Geological Survey of Nigeria.

G. J. Williams, formerly of the Survey of Gold Coast, was recently in South Africa en route to the chair of mining at Otago, New Zealand.

Donald M. Fraser, Assistant Geologist, Bethlehem Steel Company, has been appointed to the position of Chief Geologist left vacant by the recent death of W. S. Cumings.

Dr. Willis Ambrose, formerly of the Geological Survey of Canada, will be on the staff of the Department of Geology, Queen's University, for the season 1945–46.

Samuel H. Dolbear and Charles H. Behre, Jr., announce the formation of the firm of Behre Dolbear & Company, Consultants in the Mineral Industries, Mining, Metallurgy, and Geology. Their associates are H. Foster Bain, J. F. Geary, G. A. Joslin, C. C. Morfit, Walter A. Rukeyser, and Herbert Waterman, and their offices are, 11 Broadway, New York 4, N. Y., and 704 S. Spring Street, Los Angeles 14, California.

Friends of Mr. Paul Fourmarier will be pleased to hear that he is once more in correspondence with his friends abroad. Mr. Fourmarier's present address is 3F Avenue des Platanes, Counte—Sclessin lez Liege, Belgium.

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